

PROCEEDINGS  
OF THE  
NATIONAL ACADEMY OF SCIENCES  
INDIA

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VOLUME 24

SECTION—A

PART II

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PROCEEDINGS  
OF  
THE SYMPOSIUM  
ON  
RECENT TRENDS IN SOIL  
RESEARCH  
PART II

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ON  
RECENT TRENDS IN SOIL RESEARCH  
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THE TWENTY-FOURTH ANNUAL SESSION  
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PART II

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SECTION—2

SOIL MINERALOGY AND PHYSICO-CHEMICAL PROPERTIES  
OF SOILS

STUDIES IN THE BUFFERING CAPACITIES OF KASIM BAZAR,  
RAJ MAHAL AND SIMULTALA CLAYS AND AGRA SOIL  
WHEN THEY ARE HYDRATED AND HUMIFIED UNDER  
LABORATORY CONDITIONS

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(Communicated by Dr. S. P. Mitra)

*(Received on 1st October, 1954)*

The buffering capacity of the soil has been recognized as one of the most important characteristics to show the proportion of the acidoid and basoid components of the soil colloidal complex. Schofield<sup>1</sup> devised the technique of the buffer curve and studied the base uptake property at different pH values of soils by which the lime requirement at different pH could be determined. Bradfield<sup>2</sup> and Mukherji and Mittra<sup>3</sup> carried out electrometric titration of clays and observed that the manner of variation of pH of electrodialysed clay with its concentration is of the same nature as that of a weak acid like acetic acid. Consequently they drew the conclusion that the colloidal fraction of an acid soil ionises in solution giving a definite pH value which can be titrated by strong bases.



Puri and Asghar<sup>4</sup> also concluded from their result that the titration curve of soil acidoid closely resemble those of weak dibasic acids.

Ray Chaudhuri and co-workers<sup>5</sup> classified the different types of Indian soils on the result of their buffer curves studied at different pH values in the range 1.3-12.5.

In this paper we wish to communicate our investigation on the variations in the buffering capacity of three types of clays—Raj Mahal, Simultala and Kasim Bazar and of Agra soil after subjecting them to humification and hydrations for four months by raw organic matter—peepal leaves and oil cake.

#### EXPERIMENTAL

Kasim Bazar, Raj Mahal and Simultala clays and Agra soil were hydrated and humified by dry peepal leaves and oil cake as described in our previous publication.<sup>6</sup> The samples from the hydrated and humified clays and soil were taken from the pots after a period of 4 months. These were dried and sieved.

Five-gram portions of the sample were taken in flasks, each containing 15 c. c. of water, to which varying amounts of 0.1 N-hydrochloric acid and 0.1 N-sodium hydroxide, respectively had been added. After allowing to stand for 24 hour with frequent shaking, the pH was determined potentiometrically. The results were plotted taking the amounts of acid or alkali added as abscissa and the corresponding pH values as ordinates. By joining the plots, buffering curves were obtained.

In order to ascertain the buffer capacity the following procedure was adopted :—

Suppose for one sample the pH of soil + water (containing 0 c.c. acid) =  $X_1$  (1)

Suppose for that sample the pH of soil + water (containing 1 c.c. acid) =  $X_1$  (2)

and for that sample the pH of soil + water (containing 2 c.c. acid) =  $X_2$  (3)

Then change in pH between (1) and (2) =  $X - X_1$ ;

Then change in pH between (1) and (3) =  $X - X_2$  and so on.

Similarly for the other sample  $X_1 - X_1^1$ ,  $X^1 - X_2^1$  etc, will be the corresponding changes in the pH brought about under similar treatment.

The values of  $X - X_1$  and  $X - X_2$  would thus indicate the pH changes brought about by adding the soil or clay to the solutions at different pH values. Hence the buffering capacity of the one sample compared to the other would be greater if  $X - X_1$  is less than  $X^1 - X_1^1$ , and  $X - X_2$  is less than  $X^1 - X_2^1$  and so on. In table I the values of pH for soil or clay-water system by adding 0.5 c.c. of acid, and 0.5 c.c. of alkali have been recorded. In Table II the pH changes, *i.e.*,  $X - X_1$ ,  $X - X_2$  have been given. The comparative changes in pH can also be read from the buffer curves.

TABLE No. I

pH when varying amounts of acid or alkali is added

	Acid added (0.1 N HCl.)						Alkali added (0.1 N NaOH)					
	ac.c.	1c.c.	2c.c.	3c.c.	4c.c.	5c.c.	0cc.	1c.c.	2c.c.	3c.c.	4c.c.	5c.c.
	x	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>4</sub>	x <sub>5</sub>	y	y <sub>1</sub>	y <sub>2</sub>	y <sub>3</sub>	y <sub>4</sub>	y <sub>5</sub>
WATER	6.80	2.26	1.83	1.63	1.54	1.47	6.80	10.67	11.18	11.51	11.70	11.82
SOIL (original)	7.45	7.20	6.90	6.49	6.19	5.90	7.45	8.87	9.55	9.85	11.28	11.48
„ hydrated	7.50	7.06	6.85	6.55	6.49	6.13	7.50	9.31	10.78	...	11.50	11.80
„ peepal leaves	7.45	7.27	6.95	6.75	6.50	6.37	7.45	9.46	10.38	10.93	11.31	11.78
„ oil cake	6.96	6.42	6.09	6.00	5.74	5.44	6.96	7.58	8.18	9.98	...	...
KASIMBAZAR clay	6.68	6.00	3.18	2.47	2.07	2.04	6.68	9.68	10.46	10.92	11.28	11.38
hydrated.												
„ peepal leaves	7.01	7.01	6.60	6.12	4.20	3.01	7.07	9.96	10.61	11.00	11.19	11.26
„ oil cake	6.70	6.58	5.68	5.20	4.00	3.13	6.70	7.20	8.72	10.42	11.37	...
„ original	7.34	5.29	2.83	2.45	2.12	1.97	7.34	10.19	11.02	11.17	11.42	11.63
RAJMAHAL	7.43	3.90	2.33	2.01	1.87	1.77	7.43	10.00	10.46	10.90	11.10	11.23
original												
„ hydrated	7.39	3.59	2.09	2.82	1.64	1.52	7.39	10.26	11.04	11.43	11.63	11.71
„ peepal leaves	7.02	...	4.81	2.92	2.75	2.23	7.02	10.32	10.92	11.07	11.35	11.56
„ oil cake	7.43	6.33	5.72	4.77	3.49	2.88	7.43	8.01	9.91	10.90	11.41	11.54
SIMULTALA	7.08	3.65	2.54	2.34	2.16	2.10	7.08	8.12	8.78	9.70	10.00	10.56
original												
„ hydrated	7.29	2.97	2.76	2.41	2.21	2.03	7.29	8.83	10.00	10.70	10.92	11.05
„ oil cake	7.44	6.99	6.10	5.46	3.80	3.19	7.44	8.09	9.16	10.13	10.88	...

TABLE No. II

Change in pH by adding varying amounts of acid or alkali (calculated from Table I)

	Amount of acid					Amount of alkali				
	1 c. c. $x-x_1$	2 c. c. $x-x_2$	3 c. c. $x-x_3$	4 c. c. $x-x_4$	5 c. c. $x-x_5$	1 c. c. $y_1-y$	2 c. c. $y_2-y$	3 c. c. $y_3-y$	4 c. c. $y_4-y$	5 c. c. $y_5-y$
WATER	4.54	4.97	5.17	5.26	5.33	3.87	4.38	4.71	4.90	5.01
SOIL original	0.25	0.35	1.05	1.35	1.46	1.42	2.10	2.40	3.83	4.03
„ hydrated	0.44	0.65	0.95	1.01	1.37	1.81	3.28	...	4.00	4.30
„ peepal leaves	0.18	0.50	0.70	0.95	1.08	2.01	2.93	3.48	3.86	4.33
„ oil cake	0.54	0.87	0.96	1.22	1.52	0.52	1.22	3.01	...	...
KASIMBAZAR clay	2.05	4.51	4.89	5.22	5.37	2.85	3.78	3.83	4.08	4.29
„ hydrated	0.68	3.50	4.21	4.61	4.64	3.00	3.78	4.24	4.60	4.70
„ peepal leaves	0.00	0.41	0.89	2.81	4.00	2.94	3.59	3.98	4.17	4.25
„ oil cake	0.12	1.02	1.50	2.70	3.57	0.59	2.02	3.72	4.67	...
RAJMAHAL clay	3.53	5.10	5.42	5.56	5.66	2.57	3.03	3.47	3.67	3.80
„ hydrated	3.89	5.30	5.57	5.75	5.85	2.87	3.65	4.04	4.24	4.32
„ peepal leaves	...	2.21	4.10	4.27	4.79	3.30	3.88	4.05	4.33	4.54
„ oil cake	1.10	1.71	2.66	3.94	4.55	0.58	3.48	3.47	3.98	4.11
SIMULATLA clay	3.43	4.54	4.64	4.92	4.98	1.04	1.70	2.62	2.92	3.48
„ hydrated	3.32	4.53	4.88	5.08	5.26	1.54	2.71	3.41	3.63	3.76
„ oil cake	0.45	1.34	1.98	3.64	4.25	0.65	1.72	2.69	3.44	...

## DISCUSSION

In order to discuss the buffering capacity of the original clays and soil *vis-a-vis* the hydrated and humified clays with peepal leaves and oil cake, the interesting results based upon our observations are presented as follows:—

From the figures given in table II on the acid side the relative change in pH of the hydrated and humified Agra soil and clays—compared to the original samples of Agra soil and clays can be readily studied. For example, the value of  $X-X_1$  for the original soil in column 1 is .25 while the value of  $X-X_1$  for the hydrated soil is .44, which means that the hydrated soil shows less buffering than the original Agra soil. In the same way the value of  $X-X_1$  for the soil humified with peepal leaves is .18 as compared with the value for the original soil (.25). This means that the soil humified with peepal leaves assumes greater buffering capacity than the original soil on the acid side. Comparing the values in this way for the different amounts of the acids or alkali added (columns 1-10, table II) it can now be generalised thus:—

1. The hydrated soil shows less buffering capacity than the original up to the pH corresponding to 2 c.c. of acid added, after which the reverse phenomenon takes place. By comparing the figures ( $Y_1-Y$ ), ( $Y_2-Y$ ), etc. for the original and the hydrated soil it will be evident that the hydrated soil shows less buffering than the original soil on the alkali side also.

2. When the clays are hydrated, it is observed that the buffering capacity is decreased both on the acid side as well as on the alkali side except the Kasim Bazar clay which shows an increase on the acid side.

3. From the figures corresponding to  $(X-X_1)$ ,  $(X-X_2)$ , etc. for the original soil and the soil humified with peepal leaves it is observed that the peepal leaves give the soil more buffering capacity on the acid side and less on the alkali side. It is further interesting to observe that the peepal leaves exert a much stronger buffering action on the three types of clays - Kasim Bazar, Raj Mahal and Amaltala than the Agra soil on the acid side. This can be readily known from the values  $(X-X_1)$ ,  $(X-X_2)$ , etc. obtained for the original clays and those humified with peepal leaves. But the peepal leaves decrease the buffering capacity of the soil as well as of the clays on the alkali side.

4. The oil cake decreases the buffering capacity of the soil much more upto 2 c.c. of the acid after which it tends to make up at higher concentrations of the acid. But when the clays are humified with oil cake, we observe that there is a definite increase in buffering capacity on the acid side. On the alkali side the observations are more interesting. It will be clear from the figures given in table II that the soil and clays humified with oil cake show, in general, an increase in the buffering capacity on the alkali side up to 4 c.c. of alkali added and then the reverse phenomenon takes place.

The foregoing observations lead us to conclude that the peepal leaves would serve to control the pH of the soil much better on the acid side than the oil cake. On the alkali side, the buffering action of oil cake is better than the peepal leaves.

The causes of the buffering action due to the humification of clays and soil with raw organic matter cannot be explained definitely in the present state of knowledge. We can only suggest, a priori, that the proportion of acidoid and basoid components (including humus) of the clays and soils during the process of humification is responsible for the variations of buffering properties which play a very important role in maintaining acid-base equilibrium in the soil at such an optimum value as may be suitable for plant growth. This optimum, on the other hand, is specific for the nature of the plant that is grown on the soil.

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# PROPERTIES OF SOME SOILS OF WEST BENGAL : CLAY MINERALOGY IN RELATION TO CHEMICAL, ELECTROCHEMICAL AND PHYSICAL PROPERTIES

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(Received on 25th September, 1954)

Extensive researches carried all over the world have established beyond doubt that the properties of a soil are dominated to a large extent by the nature and amounts of clay materials present in them. The clay materials, *i.e.*, the fine fractions of soils having equivalent spherical diameter of particles of less than 0.00 mm, are in turn composed of one or more members of a relatively few groups of secondary silicate minerals known as 'Clay Minerals.' The common clay minerals found in soils are ; kaolinite, montmorillonite and illite. X-ray<sup>1,2</sup> optical<sup>3,4</sup> and thermal dehydration<sup>5</sup> methods have been requisitioned for the identification and quantitative estimation of clay minerals present in soils. The clay minerals are crystalline in character and their lattice structures are now fairly known.<sup>6</sup> The properties of clay minerals are intimately related to their lattice structures<sup>4,7-9</sup>. A consideration of the crystalline structures of the clay minerals reveals that kaolinites should have low base exchange capacity and as such should retain small amounts of plant nutrients but should readily give them away to plants while montmorillonites should possess a high exchange capacity as a result montmorillonites can absorb quite a lot of nutrients but part with these rather reluctantly unless the latter are present in sufficiently large amounts. Also from the same consideration it follows that montmorillonites should show swelling, shrinkage, plasticity and other properties depending on soil moisture relationship to a much greater degree compared to kaolinites and that the behaviour of illite should be intermediate between those of montmorillonites and kaolinites. These predictions are borne out by actual experiments.

A knowledge of the nature and amounts of clay minerals present in soils as also of the nature of exchangeable ions present is of vital importance in relation to their use in agriculture, constructional engineering, and in ceramic, petroleum and other industries since the chemical, electrochemical and physical properties of soils are greatly influenced by these two factors. There is however a group of colloidal properties which determine the suitability of clays for specific uses. These aspects cannot be dealt with directly by x-ray and other physical methods but these in conjunction with electrochemical methods<sup>10,11</sup> enable us to obtain fuller information.

The fundamental electrochemical character of acid clays isolated from a number of Indian soils have been studied and in some cases correlated with their mineralogical composition.<sup>11,12</sup> In view of the importance of this work, systematic investigations on the properties of typical soils of West Bengal have

been undertaken at the Bengal Engineering College along the above lines. In addition, an attempt has been made to correlate the engineering properties of these soils with their mineralogical compositions. The results of this work are likely to help us in the systematisation, classification and standardisation of the soils of the State for specific uses.<sup>27</sup> The present paper records the results obtained with three soils of the State.

The details of the methods of preparation of hydrogen clays (H-clays), chemical analysis, electrometric titration, viscometric and X-ray studies have been discussed in a previous publication.<sup>17</sup> The percentage of each soil fraction, *i.e.*, grading, has been determined according to the International method<sup>28</sup>; moisture content at saturation and volume expansion using Keen box<sup>29</sup>; shrinkage limit, shrinkage ratio, lower liquid limit, plastic limit, plasticity index and field moisture equivalent according to the method of Hogentogler,<sup>30,31</sup> and permeability coefficient using a constant head permeameter. For saturating the soil with aluminium, it was first saturated with sodium and then leached with a concentrated solution of aluminium chloride, followed by repeated washing with distilled water. Determination of the base exchange capacity as also of exchangeable aluminium of the treated soil (No. 3) showed that the latter was 92.2 per cent. saturated with aluminium. The description of the soils used as also the reference number of the corresponding H-clays have been detailed in table I.

TABLE I

No. of soil	Description of soil	Reference No. of H-clay
1	Clayey soil (0.6") collected from Hooghly, West Bengal	H-A
2	Clay Loam soil (0.6") collected from Tollygunge, Calcutta	H-T
3	Loam soil (0.6") collected from Sibpur, Howrah	H-S

The percentage of the different sized fraction, *i.e.*, grading, of the soils has been shown in table II.

TABLE II

Fraction	Soil No. 1 %	Soil No. 2 %	Soil No. 3 %
Clay	50.1	26.9	19.9
Silt	26.9	38.7	40.1
Fine and coarse sand	17.2 4.7	28.8 1.5	36.1 2.2

The percentages of MgO and K<sub>2</sub>O of the H-clays H-A, H-T and H-S, and of the clay minerals contained in them calculated on the assumption that all the potassium comes from illite having the formula,<sup>9</sup> (OH)<sub>4</sub>K<sub>1</sub>Si<sub>8-y</sub>Al<sub>y</sub>O<sub>20</sub>, where y has a value of 1.0 and that whole of magnesium comes from montmorillonite having the formula<sup>4</sup>, (OH)<sub>4</sub>Al<sub>3-34</sub>Mg<sub>0-66</sub>Si<sub>8</sub>O<sub>20</sub>, have been presented in table III.

TABLE III

H-clay	MgO %	K <sub>2</sub> O %	Montmorillonite %	Illite %	Kaolinites %
H-A	0.51	2.50	14	40	46
H-T	1.04	1.67	28	27	45
H-S	0.74	2.20	20	35	45

X-ray diagrams of the glycerol solvated calcium saturated Hooghly clay obtained using the method of Jeffries and Jackson<sup>32</sup> suggest that the approximate percentages of montmorillonite, illite and kaolinite present in this clay are respectively 10, 50 and 40. If one considers the limitations of the quantitative analysis of clay minerals by the X-ray and chemical methods, the results obtained for the Hooghly clay by the two methods seem to agree fairly well.

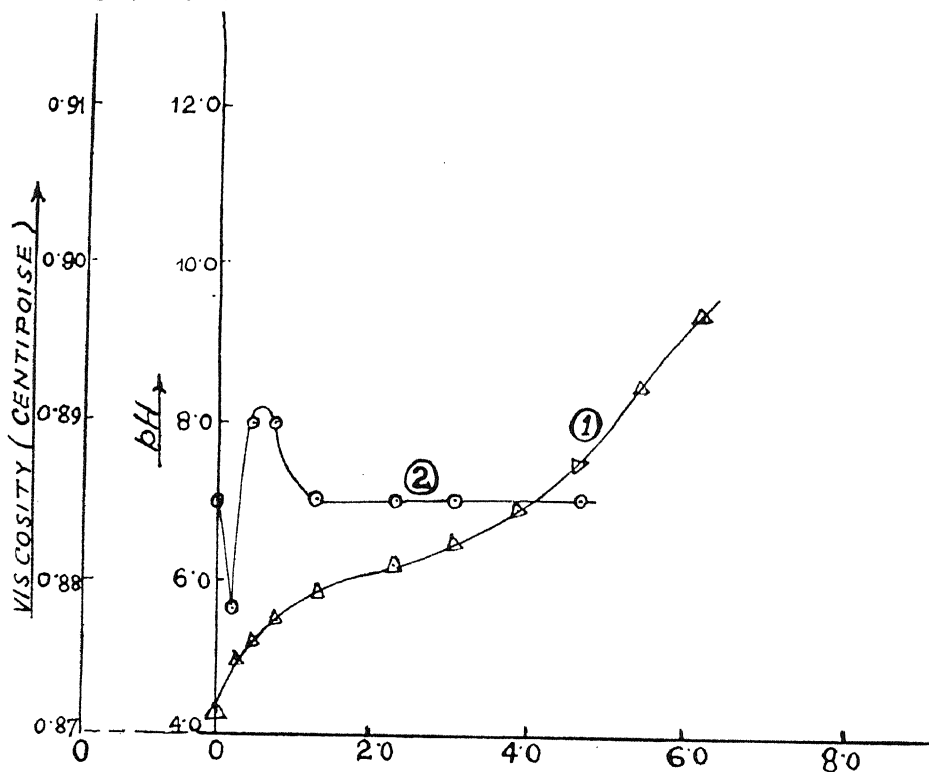


FIG. 1 MILLIEQUIVALENTS OF NaOH PER 100 GMS. OF H-A.

The presence of different clay minerals in the H-clays, H-A and H-T, as indicated by X-ray and chemical methods is also revealed in the nature of the pH-alkali concentration curves (1, 3) as also of the viscosity-alkali concentration curves (2, 4) obtained on adding increasing amounts of NaOH to the H-clays (Figs. 1 and 2). These curves while indicating the presence of montmorillonite in the two clays also suggest that illite and/or kaolinite are present in them.

The low base exchange capacity (55.0 and 44.0 milliequivalents per 100 gms. of clay) as calculated at the inflexion points in the pH alkali concentration curves as also the smaller rise in viscosity at the maximum of the viscosity-alkali concentration curves, compared to the corresponding values for pure montmorillonite, corroborate this statement.

The next phase of the present investigation consisted in the determination of the physical constants of the three soils and in the correlation of these properties with the relative proportions of clay minerals present in them. The results obtained on the physical constants of the three soils have been presented in table IV.

TABLE IV

Properties		Soil No. 1	Soil No. 2	Soil No. 3
		%	%	%
Moisture content at saturation	...	38.3	47.2	41.8
Field moisture Equivalent	...	27.0	29.6	25.6
Lower Liquid Limit	...	45.0	47.2	35.5
Plastic Limit	...	21.7	30.9	30.0
Plasticity Index	...	23.3	16.3	5.5
Shrinkage Limit	...	8.0	30.6	25.4
Shrinkage Ratio	...	1.95	1.50	1.23

The data presented in table IV bring out, at least in a qualitative manner, the effect of the relative amounts of montmorillonite contents of the three soils on the values of their physical constants. The difference in the behaviour of the soils will be more clearly elucidated if the results are compared on the basis of 100 gms. of clay instead of 100 gms. of soil (*vide* table II).

It is however observed that the physical characteristics of a soil depend not only on their clay mineralogy but also on the nature of the exchangeable bases present. It was therefore thought desirable to study the physical characteristics of a soil after saturating it with aluminium and compare the results with those of the natural soil. Aluminium ion has been chosen from physicochemical considerations<sup>10, 11, 33</sup>. This ion is expected to improve the physical properties of the soil, *i.e.*, should stabilise the soil. The results obtained with the Sibpur soil (No. 3) have been shown in table V.

TABLE V

Properties		Untreated soil	Treated soil
		%	%
Moisture Content at Saturation	...	41.8	41.9
Volume Expansion	...	7.1	6.4
Field Moisture Equivalent	...	25.6	28.0
Lower Liquid Limit	...	35.5	37.0
Plastic Limit	...	30.0	29.2
Plasticity Index	...	5.5	7.8
Shrinkage Limit	...	25.4	27.6
Permeability Coefficient	...	6.310 <sup>-4</sup>	1.010 <sup>-4</sup>



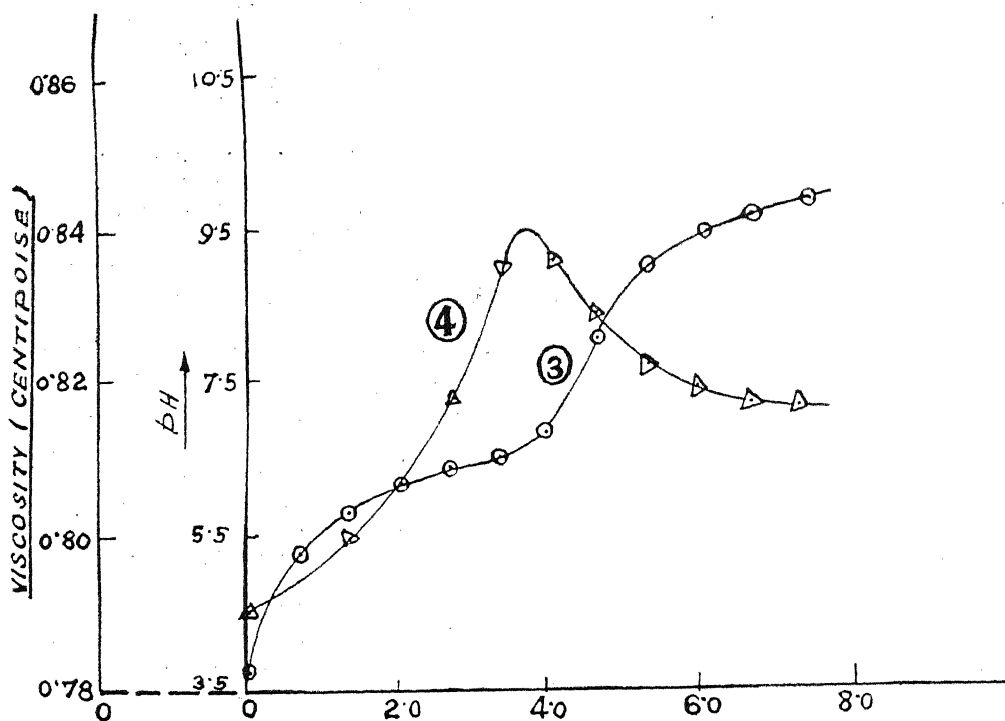


FIG. 2. MILLIEQUIVALENTS OF NaOH PER 100 Gms. H-T.

It will be observed that the improvement of the physical properties brought about on replacement of the exchangeable ions (mostly calcium and magnesium) by aluminium is not very marked excepting that the permeability coefficient is found to be much lower in the aluminium treated soil. This property in conjunction with the fact that the volume expansion of the treated soil is also less than that of the natural soil seem to attribute a higher stability against the disintegrating action of water on saturation with aluminium. This is corroborated by the observation that an air dried ball made from the untreated soil disintegrated completely into fragments in 25 minutes when placed in distilled water while 93 per cent of the ball made from the aluminium saturated soil remained in tact under these conditions. Further work on this point is in progress.

#### CONCLUSIONS

The chemical, electrochemical and physical properties of soils can be predicted, at least in a qualitative manner, from a knowledge of the relative proportions of clay minerals present in them and also of their exchangeable ions.

The data presented in this paper indicate that the soils under investigation have fair reserves of potassium and that the amounts of fertilisers applied to these should be moderate; for if too little fertilizer is applied, the montmorillonite part of these soils will absorb most of it and will not release the nutrients to the plants<sup>6,34</sup> while with abundance some of the fertilizers will be lost under moderate to heavy drainage.

The relative proportions of clay mineral present in these soil and the nature of the exchangeable bases (mostly calcium and magnesium with 1 to 2 milliequivalents of potassium per 100 gms. of soil) and their grading account, in a qualitative manner, for the observed physical properties of the soils viz, swelling, shrinkage, plasticity, hydration, etc., which are of importance in engineering enterprise. A comparison of the numerical values of the physical constants of the soils under investigation with those of the different groups<sup>31 35</sup> suggests that the soils from Hooghly, Tollvunge and Sibpur belong respectively to the A-7, A-5 and A 4 groups. The performance of a soil can be forecast in a qualitative manner, from a knowledge of the group properties. It should, however, be mentioned that in interpreting the results of soil tests, the condition of the field, its formation history, location and natural environment are taken into consideration as all these factors contribute to the performance of a soil as an engineering material. From these considerations it appears that the Sibpur soil is best suited for foundation work and Hooghly soil is fairly suitable for this purpose. Both the soils can be used for dam construction and as fill material after stabilisation by densification. These soils as such are not suitable for highway and airport construction but can be used for these purposes *only after* elaborate treatments, such as, thick macadam or concrete pavement, subgrade treatment by admixture with coarse constituents, crack, control and reinforcement, oiling, etc. The Sibpur soil may, however, form stable road when dry but will soften under moist condition. From a consideration of the group properties of the Tollvunge soil it appears that this soil should not be used for any engineering enterprise. This soil as such should be avoided, if possible, even for footings, abutments and embankments or for use as fill and dam materials. If however it is to be used for highway and airport construction, elaborate dressings such as those prescribed for Sibpur and Hooghly soils are its requirements.

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## PHOSPHATE ADSORPTION BY VERMICULITE

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The problem of phosphate fixation has largely been investigated during these years. The present investigation was undertaken with a view to examine the possibility of phosphate fixation on the surface of pure micaceous mineral like vermiculite.

In the present study attempt has been made to find out the mechanism of phosphate adsorption as well as to verify the law of adsorption in vermiculite.

### EXPERIMENTAL

The vermiculite sample used for the present study was obtained from the Bureau of Mineral Development, Government of Mysore, Mysore Geological Department, P. O. Bageshpura, District Hasan.

5 grams of vermiculite (powdered and oven-dried) were taken in 250 c. c. flasks and 100 c. c. of monocalcium phosphate solutions of different concentrations varying from 0.02 molar to 0.002 molar were added and the contents were shaken in a mechanical shaker for an hour and then allowed to stand for 24 hours at room temperature.

After the completion of the adsorption experiment, the supernatant liquid was separated from the mineral by filtering it through a buchner funnel fitted with a filter paper. The excess of ions from the mineral were then removed by washing the various samples with 40 per cent alcohol. The exchangeable cations were then determined in these samples.

### METHODS OF ANALYSIS

*Determination of phosphate*—5-20 c. c. of the supernatant liquid were pipetted in a beaker and boiled with 5 c. c. of Conc.  $\text{HNO}_3$ . The phosphate was precipitated by ammonium molybdate solution and  $\text{P}_2\text{O}_5$  estimated volumetrically.

*Determination of Calcium*—25-50 c. c. of the supernatant liquid was taken which gave a precipitate on the addition of ammonia. This is due to the presence of phosphate. The phosphate was removed by addition of 10 c. c. of sodium acetate solution and excess of acetic acid. The solution was then boiled and calcium was precipitated as oxalate and estimated volumetrically.

*Analysis of Vermiculite* The sample was finely powdered in an electric-grinding machine and passed through a 100 mesh sieve. The sample was then dried in an oven for 5-6 hours at  $105^\circ\text{C}$ . and then it was used for the chemical analysis and adsorption experiments.

2 grams of vermiculite powder was taken in a weighed platinum crucible and 10 grams of anhydrous  $\text{Na}_2\text{CO}_3$  was added to it and the whole mass was mixed thoroughly by stirring. The crucible was then heated first on a bunsen burner for an hour and then on a blower until the whole mass was in a state of quite fusion. When the decomposition was complete, the crucible was removed from the flame and cooled thoroughly. The crucible containing the cake was filled  $\frac{1}{3}$  with water and the contents were allowed to remain in contact with water overnight. Next day the cake was loosened and transferred to a platinum basin. 20 c. c. of Conc. HCl were poured very slowly into the basin. The contents were then evaporated to dryness on a waterbath. The mass was cooled and 5 c. c. of Conc. HCl were added to dissolve the basic salts of iron, aluminium, and magnesium that were formed during the evaporation. Now 100 c. c. of water were added and the basin was again heated on a waterbath till the chlorides were entirely dissolved and insoluble silica remained. The insoluble silica was filtered and washed with hot water till free from chloride ions. The volume of the filtrate was made up to 500 c. c. and the estimations of sesquioxide, iron, calcium, magnesium, potash and phosphate were made as usual.

*Conductivity Measurements*—The specific electric conductivities of the solutions used for adsorption as well as the conductivities of the supernatant liquids after adsorption have been determined according to the method given in the book "Practical Physical Chemistry," pp. 156-172 by Alexander Findlay.

*pH Measurements*—pH of the filtrates after the uptake of ions take place and of the solutions used for the study have been determined by the Beckman pH meter.

*Exchangeable Cations of the Treated Mineral*—The cation exchange reactions were carried out as follows. Several 4 gram samples were brought into contact intermittently with neutral normal solution of ammonium acetate and leached until the adsorbed cations failed to appear in the filtrates. The filtrate was then analyzed for the cations as usual.

## RESULTS

### Chemical analysis of vermiculite

1.	Loss on ignition	4.68%
2.	Silica	39.84%
3.	CaO	1.77%
4.	MgO	11.85%
5.	$\text{K}_2\text{O}$	4.45%
6.	$\text{P}_2\text{O}_5$	0.169%
7.	Sesquioxides	29.85%
8.	$\text{Fe}_2\text{O}_3$	20.4%
9.	$\text{Al}_2\text{O}_3$	9.28%
10.	$\text{SiO}_2/\text{R}_2\text{O}_3$	1.3%
11.	$\text{SiO}_2/\text{Al}_2\text{O}_3$	4.2%

The exchangeable cations present in the sample were :—

	m. c/100 gm.
Ca	27.20
Mg	27.95
K	2.27

Adsorption of  $\text{H}_2\text{PO}_4$  ions from  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  in Vermiculite.

No.	Original concentration (Molar)	Equilibrium concentration (Molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 5 gm.	% adsorption
1.	·02	·013	·0976	35·1
2.	·01	·0052	·0655	47·1
3.	·0066	·0039	·0382	41·2
4.	·005	·0033	·0261	40·4
5.	·0033	·0022	·0157	34·0
6.	·0025	·0017	·0111	32·0
7.	·002	·0012	·0098	35·2

Adsorption of  $\text{Ca}^{++}$  ions from  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

Original concentration (Molar)	Equilibrium concentration (Molar)	Amount of $\text{CaO}$ adsorbed by 5 gm. mineral	% adsorption
·02	·0043	·0851	78·3
·01	·0026	·0398	73·3
·0066	·002	·0261	72·1
·005	·0016	·0183	67·2
·003	·0014	·0103	56·6
·0025	·0013	·0063	48·4
·002	·001	·0053	46·2

Change in pH of the supernatant liquid after the uptake of ions has taken place

Concentration (Molar)	Original pH	Equilibrium pH
·02	4·1	5·3
·01	4·5	6·0
·066	4·6	6·1
·005	4·7	6·4
·003	5·0	6·8
·0025	5·2	6·9
·002	5·4	7·2

Change in the specific electric conductivity of the supernatant liquid after  
adsorption (Mhos/Cm) at 30°C

Concentration (Molar)	Conductivity of the solutions	Conductivity of the supernatant liquids
·02	$10^{-3} \times 1713$	$10^{-3} \times 933$
·01	$10^{-3} \times 948$	$10^{-3} \times 479$
·0066	$10^{-3} \times 658$	$10^{-3} \times 376$
·005	$10^{-3} \times 517$	$10^{-3} \times 464$
·003	$10^{-3} \times 3609$	$10^{-3} \times 258$
·0025	$10^{-3} \times 277$	$10^{-3} \times 255$
·002	$10^{-3} \times 235$	$10^{-3} \times 214$

Exchangable cations in the mineral after adsorption

Concentration (Molar)	Exchangeable Calcium	Exchangeable Mg.	Exchangeable Potassium
·02	54·4	28·25	2·24
·01	42·4	30·25	1·98
·0066	41·6	29·8	2·00
·005	31·2	29·11	1·9
·003	29·6	30·25	1·86
·0025	28·8	28·98	1·9
·002	28·0	28·88	1·84

DISCUSSION

The foregoing results on the adsorption of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 11\text{H}_2\text{O}$  clearly show that both the ions *i.e.*,  $\text{H}_2\text{PO}_4^-$  and  $\text{Ca}^{++}$  are being adsorbed by vermiculite. The per cent. adsorption varies from 32 - 47 at various concentrations.

Bradfield, Scarseth and Steele<sup>1</sup> (1935) stated that the fixation of phosphate depends upon three conditions overlapping in nature.

1. At pH 2 - 5 the reaction is due to the gradual formation of iron and aluminium ions and their precipitation as phosphates.

2. At pH 4·5 - 7·5 the phosphate seems to be fixed on the surface of clay minerals.

3. At pH 6-10 the phosphate is fixed largely by divalent cations if present.

As this vermiculite contains high amount of iron oxide and the pH of the solution used lies between 4 and 5, the high uptake of phosphate may possibly be due to the precipitation of iron phosphate.

Previous studies have shown that vermiculite is a mica in which  $\text{Mg}^{++}$  or  $\text{Ca}^{++}$  or both have replaced  $\text{K}^+$ . Thus it is a Mg-aluminosilicate and this sample contains Mg to the extent of 8 per cent.

Besides Fe and Al, the inorganic elements like Mg may also function to some extent in the fixation of phosphate. Fixation of phosphorus by the exchange of  $\text{PO}_4$  ions for OH ions has been reported by Mattson<sup>2</sup> (1930), Demolon and Bastisse<sup>3</sup> (1935), Scarseth<sup>4</sup> (1935), Toth<sup>5</sup> (1937), Stout<sup>6</sup> (1939), Kelley and Midgley<sup>7</sup> (1943) and Coleman<sup>8</sup> (1942).

Heck<sup>9</sup> (1934) discussed the fixation of phosphate in terms of its being unnecessary of iron and aluminium to be in solution in order to have iron and aluminium phosphate formed. According to Swensen<sup>10</sup> (1949),  $\text{Fe}(\text{OH})_2$   $\text{H}_2\text{PO}_4$  and  $\text{Al}(\text{OH})_3$   $\text{H}_2\text{PO}_4$  are formed in phosphate fixation.

From our experimental results it is seen that the amount of phosphate adsorbed by vermiculite generally decreases with an increase in pH of the solution. For this fixation of the phosphates either mechanism due to its precipitation as insoluble iron or aluminium phosphate may be possible or the phosphate fixation is due to a reversible exchange between phosphate in the solution and the hydroxyl ions in the crystal lattice.

In our experiments on adsorption it is found that the supernatant liquid has a higher pH than the original solution. This seems to be due to the liberation of OH ions in the medium from the adsorbed hydroxyl ions on the clay mineral.

So the fixation of phosphate by vermiculite may also be ascribed to a simple substitution of  $\text{PO}_4$  for OH ions.

In view of these results and all what has been discussed above the following two possibilities may be advanced in the case of phosphate uptake in minerals :—

1. Fixation of phosphate is mainly due to its precipitation by iron or aluminium present in the system.
2. Due to structural arrangements of OH in its crystal lattice.

The specific electric conductivity measurements carried out with the supernatant liquid after adsorption, show a marked decrease in the conductivities of the original solutions. This fall in conductivity points to the uptake of both the ions from the solution.

From the foregoing results it is seen that there is a marked increase in the exchangeable calcium of the system. Nearly whole of the calcium adsorbed by vermiculite enters the exchange complex and is thus easily replaceable by other cations.

It is quite interesting to note in the results that there is a slight increase in exchangeable Mg. As the exchangeability of the interlayer cations depends on their accessibility to the replacing cation, it seems that more of magnesium becomes accessible to ammonium. Besides this the greater fixation in the case of vermiculite may be attributed to the fact that the sample contains a good amount of iron oxide which readily forms insoluble phosphates.

Thus these results clearly show that vermiculite is a good adsorbent of  $\text{P}_2\text{O}_5$  and can fix a considerable amount of it. Moreover, the phenomenon of phosphate adsorption seems to be too much complicated.



#### SUMMARY

1. Vermiculite can fix  $P_2O_5$  considerably.
2. Two possibilities of this fixation may be advanced.
  - (i) Structural arrangements of OH in the crystal lattice.
  - (ii) Formation of insoluble iron, and Al phosphates.
3. Anion exchange plays a prominent role in phosphate uptake.
4. High uptake of ions may be attributed to the richness of the sample in sesquioxides and bases.
5. This adsorption obeys Freundlich adsorption isotherm in a limited range of concentration.

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## ON THE FORMOSAN CLAY

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We have seen that the soil may be conveniently considered as being composed of a relatively inert framework of unweathered minerals, and a colloidal complex consisting mainly of the products of the chemical weathering of silicates, together with humus, which is the product of the decay of plant and animal residues in the soil. By reason of the intimate association of the inorganic and the organic colloidal materials in the soil, it is convenient for many purposes to consider them as a single constituent the colloidal complex. In considering the mechanical composition of the soil, we had occasion to distinguish the so-called clay fraction, which was defined in terms of particle size. And in Japan the particle of the diameter below 0.01mm is generally called clay.

Now the clay is so minute in size, that it has some interesting properties of water-household, plasticity and base-exchange and so on. But the definition is not precise as it can comprise too many of different properties when we use the usual word clay. So we discriminate it by terming the particle below 0.001mm "colloidal clay." In this paper we wish to show some properties of the so-called clay and the colloidal clay.

### DESCRIPTION OF SAMPLES

The clay examined in this investigation was taken from various regions in Formosa.

NO. CLAY	LOCALITIES
1. Naiko clay	Naiko-sho, Sitisei-gun, Taihoku Prefecture.
2. Reisuiko clay	Sirin-sho, Sitisei-gun, Taihoku Prefecture.
3. Hokuto (gairome) clay	Hokuto-sho, Sitisei-gun, Taihoku Prefecture
4. Hokuto-sho, (with iron sand) clay	Hokuto-sho, Sitisei-gun, Taihoku Prefecture
5. Senzan clay	Oka-sho, Kaizan-gun, Kaihoku Prefecture
6. Taiko clay	Hukki-sho, Biyoritu-gun, Sintiku Prefecture
7. Nanto clay	Nanto-sho, Nanto-gun, Taitiu Prefecture
8. Sumaan clay	Gyoti-sho, Niitaka-gun, Taitiu Prefecture

### MOTHER-ROCK

1. Teritary.	5. Quarternary Basalt.
2. Quarternary Andesite.	6. Tertiary.
3. Tertiary.	7. Quarternary.
4. Quarternary Andesite.	8. Quarternary.

## EXPERIMENTAL

### (a) Clay

The samples of clay were obtained by the mechanical sieving method, using a 0.01 mm round-hole sieve. The results of chemical analysis are given in the following table :—

No.	Loss on ignition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Total
1	7.52	67.50	19.77	1.79	0.14	0.72	1.15	1.13	99.72
2	9.91	60.43	23.37	2.56	1.02	0.58	0.81	0.70	99.38
3	3.66	74.89	15.73	0.93	0.24	0.47	1.73	2.40	100.05
4	6.42	66.40	18.64	3.36	0.11	0.53	2.18	1.94	99.58
5	9.43	66.37	17.11	4.79	0.21	0.65	0.71	0.87	100.14
6	7.80	70.28	17.69	2.47	0.26	0.22	0.85	0.48	100.05
7	8.45	65.11	15.62	6.97	0.46	0.57	1.64	1.35	100.17
8	7.46	65.50	23.35	0.15	0.44	1.02	1.10	0.92	99.94

### *Heat of wetting and hygroscopicity*

We have shown in the previous paper the co-relation between heat of wetting and other important nature of the soil, and this time our interest were mainly paid on the same factor of the Formosan clay. Heat of wetting was measured by the Janert's method,<sup>2</sup> and hygroscopicity was determined by the Mitscherlich's method.<sup>3</sup> The results are as follows :—

No.	Heat of wetting	Hygroscopicity	Heat of wetting × 2
1	3.24	5.59	6.48
2	4.91	10.83	9.82
3	1.06	2.13	2.12
4	2.78	4.97	4.56
5	2.79	6.04	5.94
6	2.25	3.39	4.50
7	3.43	7.52	6.86
8	1.99	4.34	3.98

Measuring shows that Zunker's theory<sup>4</sup> that hygroscopicity is approximately given by multiplying the heat of wetting with factor 2, also holds good in this case.

### *Degree of swelling and absorption of ammonia*

The degree of swelling determined by Anderson's method<sup>5</sup> is given in the following table :—

Sample No.	1	2	3	4	5	6	7	8
Degree of swelling	22.5	48.2	52.0	52.0	38.4	33.3	17.4	15.4

The amount of ammonia absorbed by 1 gr. of clay is determined under the condition of 20 c. 1 atm.

No.	after 1 day	after 2 days	3 days	4 days	5 days	6 days
1.	41.3	41.6	41.6	42.2	42.3	42.6
2.	54.1	60.8	60.8	63.6	63.9	64.3
3.	20.2	20.3	20.0	19.9	20.2	20.2
4.	15.2	16.1	16.3	17.4	17.4	17.6
5.	27.9	32.2	32.3	33.8	33.9	33.9
6.	23.2	23.2	23.4	24.0	24.0	24.4
7.	34.0	37.1	37.3	39.0	39.0	39.2
8.	18.8	22.6	22.7	22.7	22.8	22.8

(b) Colloidal clay

The samples of colloidal clay were separated by the setting velocity method, to settle for 24 hours, after thorough agitation, the suspension were then the upper 8 cm. was siphoned off.

$\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  contents of the colloidal clay were determined by hemical analysis. As the result the following table was obtained :—

No.	$\text{SiO}_2$ %	$\text{Al}_2\text{O}_3$ %	$\text{Fe}_2\text{O}_3$ %	$\text{SiO}_2/\text{R}_2\text{O}_3$
1.	46.71	28.73	6.77	2.40
2.	45.11	16.12	20.21	2.64
3.	47.97	30.05	2.31	2.58
4.	45.21	19.98	16.73	2.52
5.	42.14	26.49	11.53	2.11
6.	45.99	26.75	12.70	2.24
7.	42.11	24.48	10.08	2.31
8.	49.21	29.44	3.67	2.63

The  $\text{SiO}_2/\text{R}_2\text{O}_3$  ratio varied from 2.11 to 2.64, and we could not find remarkable geological and constitutional meanings.

Results of X-ray study

X-ray diffraction patterns from all the colloid samples described in this paper were obtained by the use of copper radiation. The powdered materials were pasted to the fine soft glass tube and were exposed 10 hours in cylindrical camera having a radius of  $28.62 \pm 0.03$  mm.

From measurements of the patterns, interplaner spacings were calculated, using the Bragg's condition  $2d \sin \theta = n\lambda$ . The results are presented in the following table :—

Sample No.	1. $dhkl$ °	2. $dhkl$ °	3. $dhkl$ °	4. $dhkl$ °
Spectrum No.	Intensity A	Intensity A	Intensity A	Intensity A
1.	...	m. 7.20	m. 7.20	...
2.	v. s. 4.44	s. 4.30	s. 4.39	v. s. 4.44
3.	...	w. 3.56	m. 3.63	...
4.	m. 3.33*	...	s. 3.36*	m. 3.30*
5.	s. 2.56	s. 2.53	s. 2.56	v. s. 2.56

Sample No.	1. <i>dhkl</i>	2. <i>dhkl</i>	3. <i>dhkl</i>	4. <i>dhkl</i>
Spectrum No.	Intensity Å	Intensity Å	Intensity Å	Intensity Å
6.	...	w. 2.34	v. w. 2.38	...
7.				v. 2.19
8.	w. 1.98	v. w. 1.97	m. 1.97	m. 1.99
9.	s. 1.71	v. w. 1.70	v. w. 1.72	w. 1.73
10.	m. 1.66	m. 1.67	w. 1.65	w. 1.67
11.	w. 1.50	m. 1.50	m. 1.50	s. 1.50
12.				
13.	v. w. 1.28	w. 1.30		w. 1.30
Types of Clay	Bentonite	Halloysite	Halloysite	Bentonite

Sample No.	5. <i>dhkl</i>	6. <i>dhkl</i>	7. <i>dhkl</i>	8. <i>dhkl</i>
Spectrum No.	Intensity Å	Intensity Å	Intensity Å	Intensity Å
1.		m. 7.20		
2.	s. 4.39	v. s. 4.35	s. 4.33	s. 4.44
3.	...	m. 3.56		
4.	m. 3.40*		m. 3.37*	v. s. 3.36
5.	s. 2.56	s. 2.56	m. 2.56	s. 2.56
6.	...	w. 2.37		
7.	...			v. w. 2.18
8.	v. w. 1.97	w. 1.99	w. 2.01	w. 1.97
9.	...	w. 1.70	v. w. 1.70	v. w. 1.70
10.	m. 1.67	w. 1.64	w. 1.67	m. 1.67
11.	w. 1.50	w. 1.50	w. 1.50	m. 1.51
12.				v. w. 1.38
13.				v. w. 1.28

	Bentonite	Halloysite	Bentonite	Bentonite
Type of Clay				

Symbols.	*Quartz spacing	v. s. very strong
	s. strong	m. medium
	w. weak	v. w. very weak

In comparison with suitable data for known substances, which was done by Hendrick and Fry,<sup>6</sup> or Nagelschmidt,<sup>7</sup> it was recognized that these samples belong to either one or the other of the two types, namely Halloysite and Bentonite. So we can find two types of clay in Formosa.

Ultimate pH, exchange capacity, electrokinetic potential and isoelectric point.

The colloidal clay was dialysed in Mattson's cell,<sup>8</sup> and then the pH was measured. (Ultimate pH). Exchange capacity, was determined by the use of potentiometric titration. Electrokinetic potential was calculated from the migration velocity of the suspended particle, measured in the Mattson's electrocataphoresis cell,<sup>9</sup> and the isoelectric point was also measured in that cell. The results are listed in the following table :—

No.	pH of the suspension	Ultimate pH	Exchange capacity mili eq/100 gr	Electrokinetic potential millivolt		Isoelectric point
				$c=4\pi$	$c=6\pi$	
1.	6.11	3.21	21.5	$44.1 \pm 1.30$	$66.0 \pm 1.94$	2.02
2.	5.35	3.32	14.5	$34.5 \pm 0.84$	$51.6 \pm 1.25$	2.16
3.	7.36	2.90	14.9	$23.5 \pm 0.50$	$35.2 \pm 0.75$	2.40
4.	5.59	3.16	21.1	$29.8 \pm 0.49$	$44.5 \pm 0.73$	2.23
5.	5.85	3.39	28.3	$37.8 \pm 1.09$	$56.5 \pm 1.63$	2.76
6.	5.48	3.12	23.7	$42.5 \pm 0.80$	$63.6 \pm 1.20$	1.81
7.	6.07	3.14	43.0	$38.8 \pm 1.24$	$58.0 \pm 1.85$	1.71
8.	5.48	3.44	25.5	$36.3 \pm 0.88$	$54.2 \pm 1.31$	2.61

The pH of the suspension are always greater than the isoelectric point. In view of this fact, the Formosan clay is so chemically unstable that when the electrolyts are leached, the potential of the particle will increase, and thus the particle will run off.

The suspensions are more always reacted by alkaline medium than its isoelectric point, and so the possibility of the silicate partially changed in colloidal state will increase. So in the weathering of the clay we can expect some clay abundant in  $R_2O_3$ .

#### SUMMARY

In this investigation of ours, 8 samples of clay in Formosa were studied. From our study of the clay and the colloidal clay we have reached to the following conclusion.

In Formosa, we can find two types of clay, namely halloysite and bentonite. But they can not be said to be very stable, as they have a possibility of changing their composition into the clay of increased  $R_2O_3$ .

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## ESSAIS DE PEDOLOGIE EXPERIMENTALE

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Il nous est apparu que les observations effectuées dans le milieu naturel ne permettaient pas toujours d'établir d'une manière suffisamment sûre les mécanismes expliquant les phénomènes observés. Nous avons alors cherché à compléter les méthodes purement déductives caractérisant l'histoire naturelle en introduisant systématiquement l'expérience en pédologie.

Il fallait pour cela prouver que les phénomènes peuvent être suffisamment accélérés pour être reproduits commodément et rapidement. Le simple fait de pouvoir réaliser un tel programme de recherches conduit déjà à mettre en évidence l'efficacité de certains facteurs de la pédogénèse et les conditions nécessaires à leur action.

Les recherches entreprises concernent trois groupes de faits je les énumérerai dans l'ordre suivant lequel elles ont été entreprises qui n'est pas nécessairement l'ordre logique :

- Etude sur la transformation et la formation des minéraux argileux.
- Etude expérimentale de l'altération des roches.
- Etude expérimentale sur la formation des profils.

*Etude concernant les argiles :*

(a) *Transformation des minéraux argileux.*—La structure des minéraux argileux et les observations dans le milieu naturel montrent qu'il doit y avoir un passage relativement facile de certains types de minéraux argileux à d'autres.

Nous avons essayé de reproduire expérimentalement certains d'entre eux, voici les résultats qui ont été obtenus :

en précipitant certains hydroxydes, en particulier de magnésium au contact d'une montmorillonite, tout ou partie de l'hydroxyde se dépose entre les feuillets du minéral et l'on obtient alors une chlorite gonflante. Par un traitement acide il est possible de réaliser la transformation inverse. Une telle transformation est également possible en partant de chlorites gonflantes "naturelles" qui donnent alors des montmorillonites. Cette expérience a été relaisée en utilisant des chlorites gonflantes extraites de minerais de fer et d'une marne du Keuper.

De même par ébullition d'une montmorillonite en présence de potasse on peut bloquer les feuillets de ce minéral et obtenir une substance voisine de l'illite. Inversement des micas finement broyés ont pu par l'ébullition prolongée en présence de chlorure de magnésium donner de la vermiculite et de la montmorillonite.

Nous nous limiterons à des exemples correspondant aux résultats les plus typiques.

(b) *Synthèse des minéraux argileux* :—Il est évident que les minéraux argileux peuvent se former dans les conditions de surface et plus précisément dans les sols. Cependant, nous n'avons jamais pu obtenir de minéral argileux en faisant simplement vieillir des complexes silico-alumineux ou ferrique, obtenus à froid, même à 100°, et pendant un an.

Nous avons alors opéré en faisant tomber lentement (20 à 30 cc 3 par jour) dans un ballon maintenu à l'ébullition les solutions très diluées, de concentration voisine de celle de l'eau de drainage (de l'ordre de 10 mmg par litre), de silice et des solutions de chlorure de magnésium, provenant d'un autre flacon, à des dilutions du même ordre. Dans ces conditions on obtient en opérant à des pH de l'ordre de 8 et plus des produits de types montmorillonitiques. Le même résultat a été obtenu en utilisant des sels de fer. On peut introduire de petites quantités d'alumine soit sous forme d'aluminate mélangé aux silicates soit sous forme de chlorure mélangé aux magnésium ; mais jusqu'à présent il n'a jamais été possible de faire un produit purement alumineux. Quand on abaisse le pH on obtient avec le magnésium des produits colloïdaux ou mal cristallisés et avec le fer des oxydes ou hydroxydes.

Si l'on introduit directement dans le récipient maintenu à l'ébullition une solution à 5, g. par litre de chlorure de magnésium et 50 g de chlorure de sodium il se forme alors une antigorite. La silice nécessaire à cette synthèse provient alors de l'attaque du ballon dans lequel s'effectue l'opération. Ce fait nouveau établit la possibilité d'effectuer ces synthèses à partir d'éléments à l'état solide, donc de minéraux.

Ces résultats permettent de se faire une idée générale des conclusions obtenues au cours de ces recherches. Nous n'entrerons pas dans le détail, soulignant seulement qu'il est possible d'effectuer la synthèse de certains minéraux argileux dans des conditions voisines de celles qui règnent dans le milieu naturel. Ces travaux se poursuivent avec le double but de préciser les conditions de formation des minéraux déjà synthétisés et d'autre part, d'effectuer les synthèses qui n'ont pu encore être réalisées.

#### *Altération des roches :*

P. Birot a montré que l'on peut assez facilement provoquer la désagrégation de roches éruptives par des alternatives de dessiccation (à 80°) et d'humectation. Au cours de cette évolution outre du sable il y a formation de minéraux argileux de type montmorillonitique ceci aussi bien avec des granites que des gabbros.

Le fait qu'il se forme des argiles par attaque du verre fournit une explication de ces résultats mais dans les cas observés jusqu'à présent ce sont surtout les feldspaths qui sont altérés et paraissent donner de l'argile. D'ailleurs l'altération des roches dépend dans une large mesure de la nature des électrolytes présents dans le milieu. Ainsi se trouvent reliées les expériences concernant la synthèse des minéraux argileux et l'altération des roches.

#### *Etude expérimentale sur la formation des profils :*

Les roches sédimentaires et les matériaux meubles formés par altération des roches éruptives se transforment en sols sous l'influence de divers processus biologiques et physico-chimiques. Nous nous sommes efforcés de provoquer l'évolution de certains matériaux homogènes ; au laboratoire d'abord puis en plein champ.

Le simple lessivage par l'eau ne peut guère provoquer que des entraînements de colloïdes en l'absence de calcaire, il faut même une certaine désaturation du milieu, si le milieu contient des sels des ions sodium, et surtout s'il n'est pas trop



riche en argile. Dans la nature la désaturation est une conséquence de la décomposition de la matière organique par fermentation.

Au lieu de faire percoler les tubes renfermant le matériel homogène par de l'eau on a utilisé des solutions contenant du sucre et un aliment azoté. Dans ces conditions il se produit des développements microbiens au bout de quelques jours, amenant une réduction du matériel avec formation de gley et mise en solution du fer et du manganèse. Ces éléments reprécipitent dès que les conditions du milieu deviennent oxydantes. Le phénomène se produit même en milieu calcaire, mais la précipitation en milieu oxydant est alors beaucoup plus énergique. S'il existe de la silice colloïdale, de l'humus en abondance, ou un peu de phosphate de calcium dans le milieu les mouvements du fer sont retardés ou même complètement bloqués.

Des matières organiques plus complexes telles que du foin de luzerne permettent d'obtenir des résultats du même ordre mais moins rapidement qu'avec le sucre.

Ces essais ont été repris dans le milieu naturel en délimitant de petites surfaces de sol par des cylindres d'aluminium. On obtient des résultats de même nature mais plus difficilement.

Il est surprenant de constater avec quelle facilité le fer reprécipite dès que l'on ne se trouve plus dans le volume délimité par le cylindre d'aluminium. Dans un sol en place en bon état physique les conditions sont donc franchement oxydantes en dépit de l'humidité élevée de la terre au cours des expériences.

Un des facteurs qui a le plus perturbé ces essais a été la microfaune. Des espèces assez diverses se sont rassemblées dans la zone affectée par les expériences ; il faut signaler particulièrement les fourmis et les vers de terre. La zone de terre travaillée par les animaux était surmontée par des dépôts de fer montrant l'influence qu'avait eu ce travail sur l'aération du milieu.

#### CONCLUSIONS

Ces expériences montrent qu'il est possible de reproduire au laboratoire des phénomènes de pédogénèse à condition de les accélérer en augmentant l'intensité de certains facteurs de l'évolution. Les résultats obtenus ont permis de confirmer certaines observations ; par exemple : la nécessité d'un pH relativement élevé pour former la montmorillonite, la non formation d'un silicate ferrique aux bas pH etc. . . Ils ont permis de mettre clairement en évidence le rôle retardateur des anions complexants sur les phénomènes de pédogénèse et de confirmer le rôle capital de la microfaune. Des observations complémentaires ont pu être effectuées au cours de ces essais concernant en particulier la variation de la susceptibilité magnétique des sols. En résumé, nous pensons que la méthode expérimentale, en pédologie comme ailleurs, permettra tout d'abord de préciser les connaissances acquises et permettra par la suite de mettre en évidence des faits nouveaux que l'observation seule aurait été impuissante à dégager du moins aussi rapidement.

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# ELEKTRONENMIKROSKOPISCHE UNTERSUCHUNGEN ÜBER DEN TON-HUMUS-KOMPLEX

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Über die Wechselwirkung zwischen Ton und Huminsäuren bei der Struktur-  
bildung sind von den verschiedenen Autoren Arbeitshypothesen aufgestellt worden,  
die wie folgt zusammengefasst werden können :

1. Die Festlegung der freien Huminsäuren
2. Die Alkali—, Erdalkali—und Schwermetallhumate als Klebstoffe
3. Gemische von Gelen der Oxyhydrate von Eisen und Aluminium
4. Direkte Adsorption durch Tonminerale
5. Ton-Humus-Komplexbildung
6. Bindung durch Kationenumtausch auf Tonoberflächen
7. Wechselseitige Adsorption durch bereits adsorbierte Kolloide an Ton-  
mineralen
8. Aktivierung der Adsorption durch Ioneneintausch von Schwermetallen  
an Tonen
9. Ton-Humusverbindungen auf biologischem Wege

Der Nachweis der hier aufgezählten Möglichkeiten der Wechselwirkungen  
wird aus methodischen Gründen erschwert. Wir haben uns mit Hilfe des Elek-  
tronenmikroskops bemüht, einiges zu dem erwähnten Fragenkomplex beizutragen,  
worüber in folgendem zusammenfassend berichtet werden soll.

Im Elektronenmikroskop erscheinen die Huminsäuren, wie wir schon früher  
gezeigt haben<sup>1</sup>, als Zusammenballungen von kugelförmigen Teilchen. (Abb. 1).  
Wird die Wasserstoffionenkonzentration mit Alkalien zum Neutralpunkt hin vers-  
choben, so nimmt die Grösse der Flocken ab und sie zerfallen in kleinere Gebilde.  
Wir vermuten, dass die Huminsäureteilchen durch Wasserstoffbrücken zusammen-  
gehalten werden bzw. sich mit Wasserhüllen umgeben und Coacervate bilden<sup>2</sup>.

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\*Anschrift : Braunschweig, Bundesallee, 50.

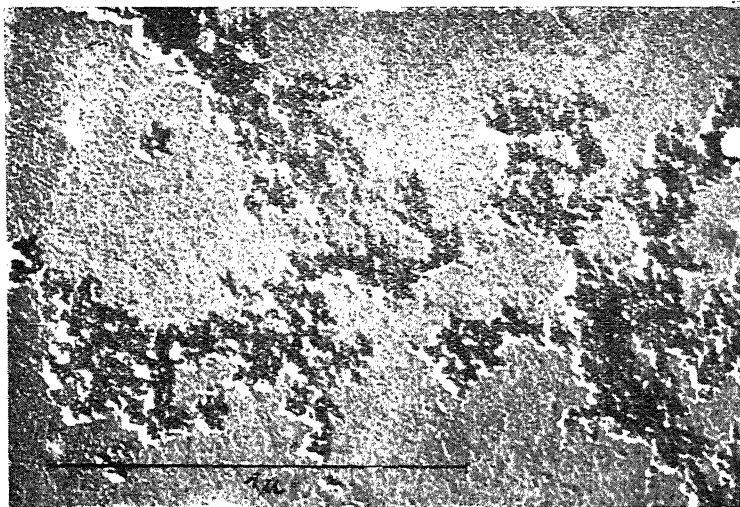


Abb. 1. Elektrodialysierte Huminsäuren bei pH 3,8 aus Schwarzerde (4+ mal mit 0,1% NaOH peptisiert und N/1 HCl ausgefällt)

Die Aufnahme in Abb. 2 zeigt dieselben Huminsäuren bei einer nur 8-maligen Umfällung. Diese Reinigung des Präparats hat nicht ausgereicht, denn wir finden noch beachtliche Verunreinigungen an Tonmineralen, die wir an den scharf umgrenzten Plättchen erkennen. Die Tone werden bei der Alkalibehandlung der Huminsäuren auch peptisiert und später beim Ausfällen mit Säuren zum Teil wieder koagulierte. Eine Adsorption der Huminsäuren an den natürlichen Mineralbeimengungen ist weder an den durchstrahlbaren Plättchen noch an den Kanten zu erkennen. In diesem Zusammenhang taucht die Frage auf, ob bei der Erforschung des sogenannten Ton-Humus-Komplexes die anorganischen Verunreinigungen nicht zu falschen Schlussfolgerungen geführt haben.

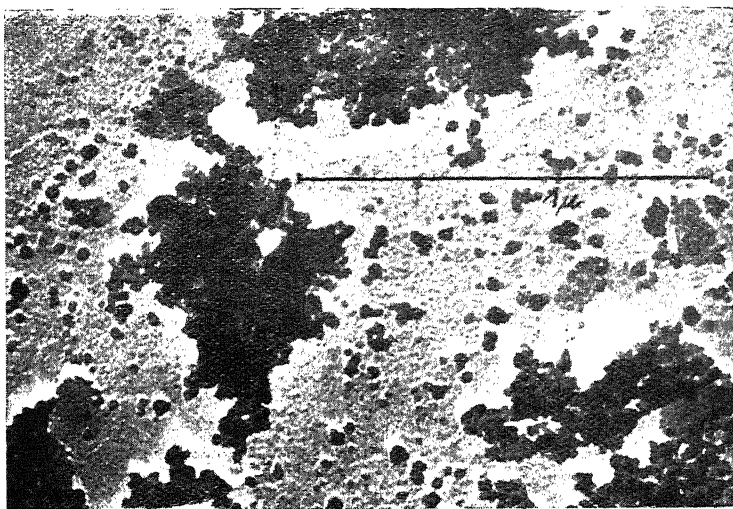


Abb. 2. Nur 8mal umgefällte Huminsäuren aus Schwarzerde

Nachdem wir zeigen konnten, dass die Humate im Gegensatz zu den reinen Huminsäuren kein elektrokinetisches Potential<sup>3</sup> besitzen, gelang uns eine fraktionierte Teilfällung mit sämtlichen Alkalisalzen. Die gefällten Alkalihumate unterschieden sich von den Huminsäuren durch kleinere Flocken, die bei sorgfältiger Dialyse als Einzelteilchen im Bild (Abb. 3) zu erkennen sind.

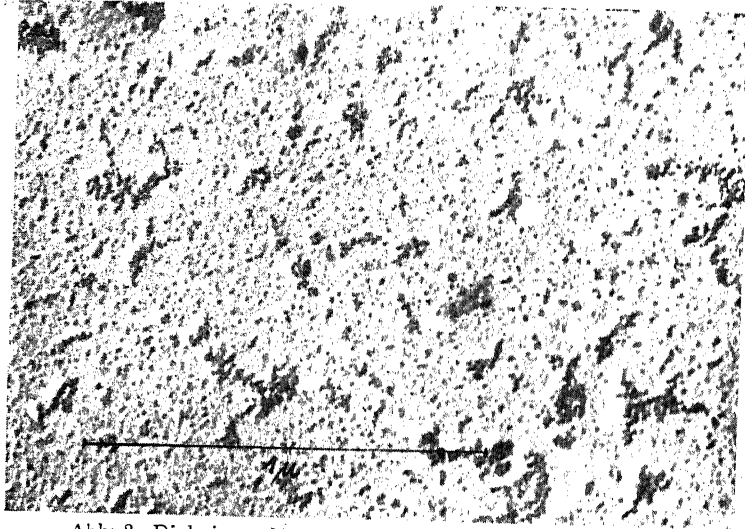


Abb. 3. Dialysiertes Natriumhumat, mit Pt. schräg bedampft

Zu den wichtigsten Kittsubstanzen bei der Krümelbildung zählt A. Tjulin<sup>4</sup> die Calciumhumate, während die Eisenhumate Aggregate von geringer Stabilität bilden sollen. Im elektronenmikroskopischen Bild unterscheiden sich die Erdalkalihumate von den Schwermetallhumaten durch eine lockere Packung der Flocken, die teilweise beim Entzug des überschüssigen Fällungsmittels zu kleineren aufpeptisierten.

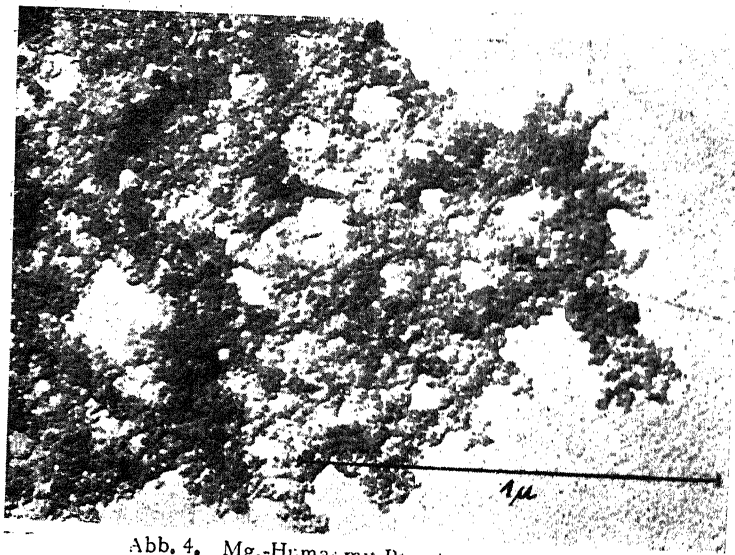


Abb. 4. Mg.-Humat mit Pt. schräg bedampft

Verschiedene Aluminium—bzw. Eisensole auf Kollodiumfolie präpariert, zeigen eine gleichmässige Verteilung (Abb. 5). Werden die gut gereinigten Sole mit Huminsäuren suspendiert, so sind in den Koagulaten die Teilchen durch den Ladungsausgleich innigst vermengt. Eine Adsorption an den verschiedenen Beyeritkristallen können wir an den durchstrahlbaren Basisflächen und Kristallkanten nicht beobachten.

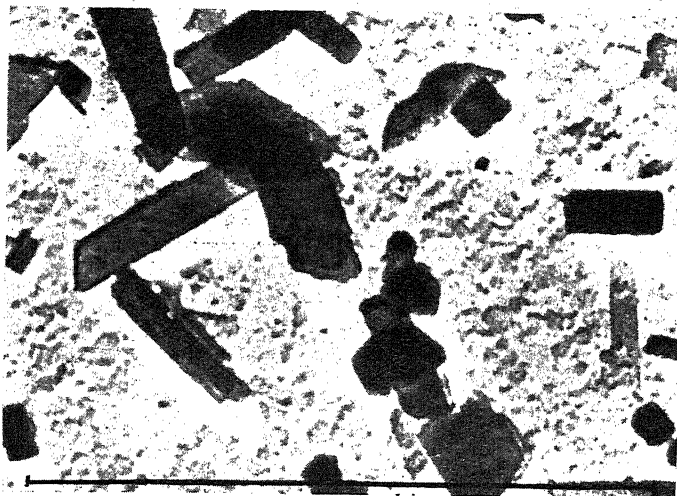


Abb. 5. 3 Jahre gealtertes  $\text{Al}(\text{OH})_3$ -Sol Beyerit

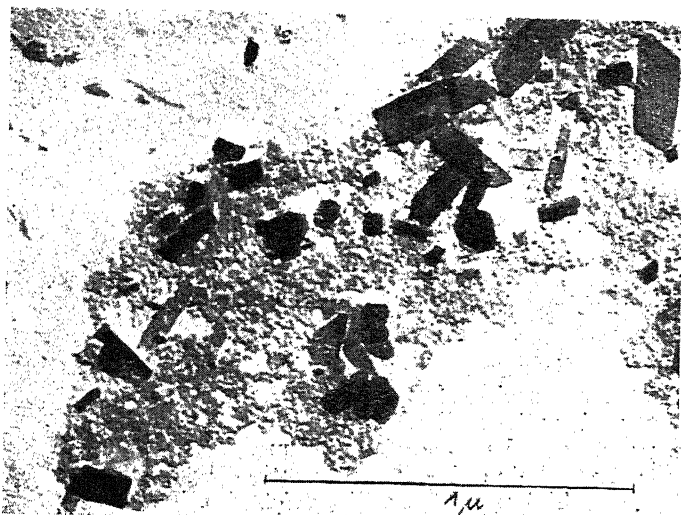


Abb. 6. Beyerit mit Huminsäuren gefezelt

Den Adsorptionsmechanismus deutet E. Gapen<sup>5</sup>, durch Veresterung der Carboxylgruppen der Huminsäuren mit den Tonmineralen. E. Jung<sup>6</sup>, glaubt

an Hand von Viskositätsmessungen eine direkte Adsorption der beiden Kolloidarten beweisen zu können. D. Sideri<sup>7</sup>, hält eine chemische Reaktion zwischen Huminsäuren und Mineralteilchen für unmöglich. Er kommt auf Grund von lichtmikroskopischen Betrachtungen zum Ergebnis, dass die Humate durch die Tone orientiert und auf ihnen abgelagert werden. Durch die irreversible Koagulation beim Eintrocknen sollen dann die Teilchen zu Krümeln verkitten.

Wir haben verschiedene Standardtone mit Huminsäuren bzw. Humaten suspendiert, schonend an der Luft getrocknet und im Elektronenmikroskop aufgenommen. Am Beispiel des Gemisches von Kaolinit und Huminsäuren (Abb. 7) sehen wir, dass weder eine Orientierung noch eine Adsorption der Huminsäureteilchen im elektronenmikroskopisch sichtbaren Bereich stattfand. Auch den Einbau der Huminsäureteilchen zwischen die Schichtpakete des Montmorillonits konnten wir nicht beobachten, halten dies auch auf Grund ihrer Teilchengrößen nicht für möglich.

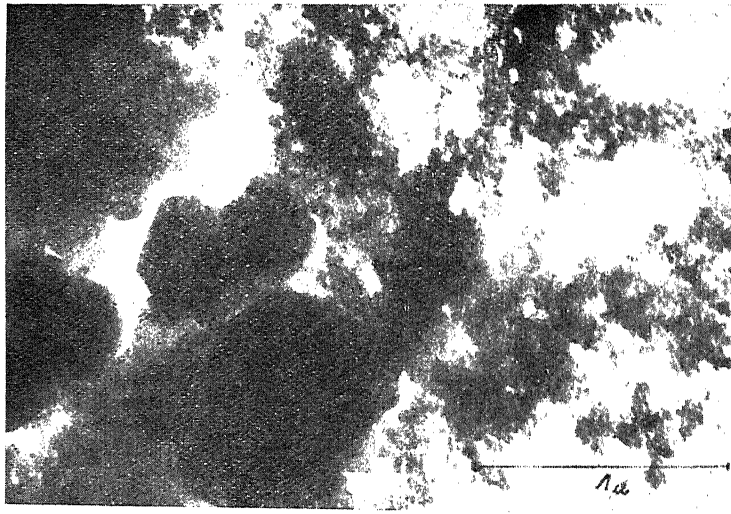


Abb. 7. Suspension von Kaolinit und Huminsäuren

Die Basisflächen der Tonminerale zeigen bei der Behandlung mit alkal. Humat an verschiedenen Stellen eine Anhäufung von Huminsäureteilchen, die wir auf Kationenumtausch an Störstellen der Kristalle und Koagulation der Humate beim Eintrocknen zurückführen.<sup>1</sup>

Untersucht man die verschiedensten Bodensuspensionen im Elektronenmikroskop, so beobachtet man meist, dass an Tonmineralen unter anderem kolloidales Eisen festhaftet und auf mechanischem Wege nicht entfernt werden kann<sup>8</sup>. Versucht man positiv geladene Eisenkolloide mit den verschiedenen Standardtonen zu mischen, so konnte keine direkte Adsorption beobachtet werden. Auch die Versuche von P. A. Thiessen,<sup>9</sup> der die wechselseitige Adsorption von Goldkolloiden und Tonen im Elektronenmikroskop nachzuweisen glaubte, konnten wir an einem grossen Material nicht beitätigen, trotz verschiedener variationsbedingungen bei der Präparation.

Um die in der Natur stattfindende Adsorption von Eisenkolloiden an Tonen in Laboratoriumsversuchen nachzuweisen, hatten wir diese mit Ferrosalzen in der

Tonsuspension durch Luftoxydation zu erzeugen versucht. Die Präparate wurden nach einer Einwirkungszeit von 60 Minuten 10-mal hintereinander mit dest. Wasser dispergiert und von der überschüssigen Eisermenge durch Zentrifugieren befreit. Aus der (Abb. 8) ist zu ersehen, wie das stäbchenförmige Sol aus Ferrochlorid auf dem durchstrahlbaren Kaolinit-Kristall haftet. Im Gegensatz zum braunen Eisenkolloid wurde aus  $\text{Fe}_2\text{SO}_4$  ein rotes gewonnen, das auf dem Pyrophyllit (Abb. 9) regelmässig verteilt war. Nach den bis jetzt vorliegenden elektronenmikroskopischen Beobachtungen scheinen die elektrokinetischen Kräfte der Tonminerale nicht auszureichen, um Kolloide direkt zu adsorbieren. Werden aber Metallionen von ihnen erst adsorbiert, so bilden sich auf den Oberflächen Kristallisationskeime in kolloidalen Dimensionen aus, die trotz mechanischer Eingriffe fest an den Tonteilchen haften und vermutlich zur Adsorption der Huminsäuren befähigt sind.

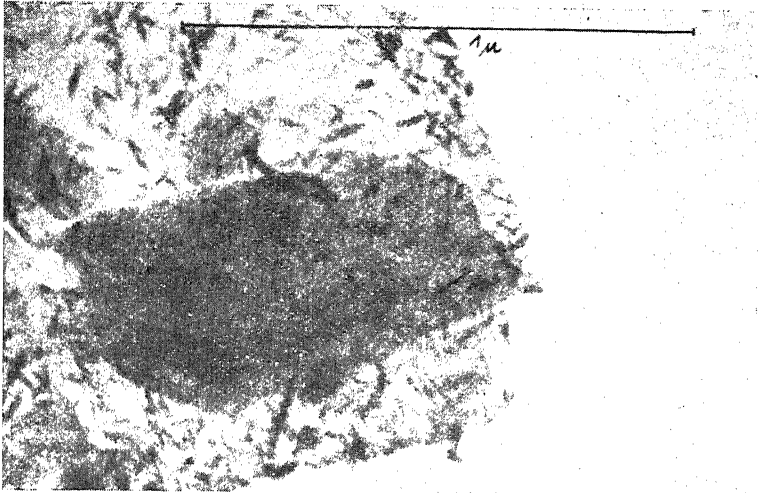


Abb. 8. Adsorption von braunem Eisensol am Kaolinit

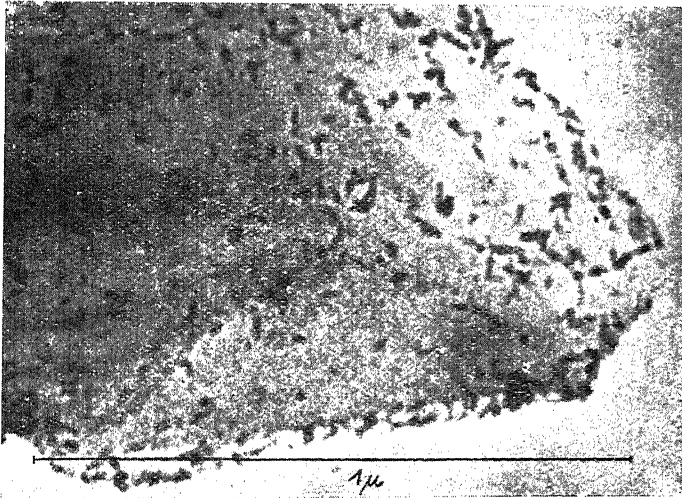


Abb. 9. Adsorption von rotem Eisensol am Pyrophyllit



Direkte Adsorption der Humate konnten wir beim Montmorillonit beobachten und auch quantitativ messen, wenn wir ihn mit Eisen aktivierten (Fe-Montmorillonit).

Nach den bis jetzt vorliegenden elektronenmikroskopischen Untersuchungen scheint es so zu sein, dass die Huminsäuren als Sphärokolloide sich als Kittsubstanzen nicht wesentlich beteiligen, sondern diese Aufgabe anderen Kolloiden im Boden zufällt. Einige Arbeiten weisen darauf hin, dass Schleimstoffe der Bakterien aber auch Pilzmycel die Primärteilchen verkleben und wasserbeständige Krümel bilden sollen. In Abb. 10 sieht man, wie die Bakteriengeißeln Kaolinitteilchen umschlingen und zusammenhalten.

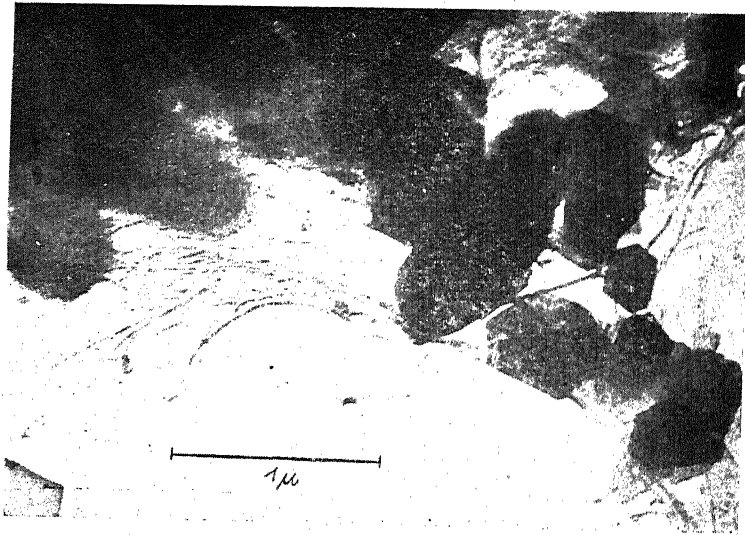


Abb. 10. Zusammenhalt von Kaolinitteilchen durch Bakteriengeißeln und-Schleim

Nach Swaby<sup>10</sup> könnten im Darmtrakt der Kleintiere die Humate mit den Bodenteilchen in innigste Verbindung gebracht werden und auf diese Weise stabile Krümel erzeugen. Wir haben frische Regenwurmausscheidungen mit Wasser dispergiert und die Suspensionen elektronenmikroskopisch untersucht. Neben zahlreichen Sphärokolloiden fanden wir Linearkolloide, die die einzelnen Tonteilchen miteinander verbinden (Abb. 11). Wir glauben, dass die Stabilität der Krümel des Regenwurmkotes auf diese fadenförmigen Kolloide zurückzuführen sind, die als Klebsubstanzen dienen.

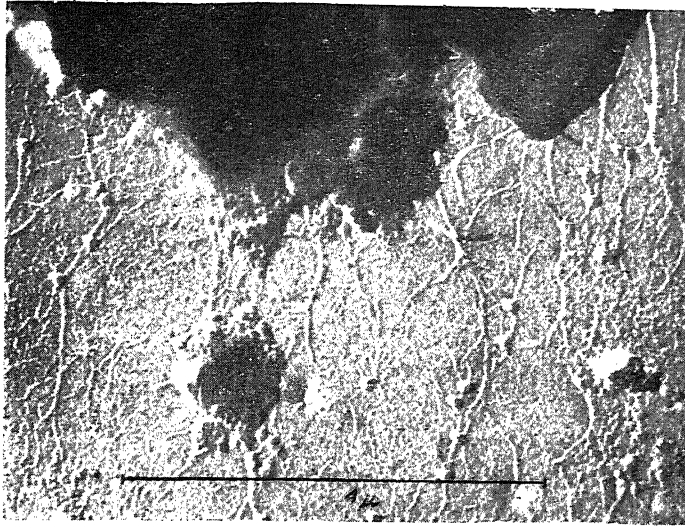


Abb. 11. Linearkolloide im Regenwurmkot

Denn an empirischen Versuchen hat man festgestellt, dass fadenförmige Kolloide befähigt sind, die Tonteilchen des Bodens in stabile Krümel umzuwandeln. Für diese Zwecke wird die Anwendung von Krilium propagiert. Werden Tonminerale mit Kriliumlösungen unter gewissen Versuchsbedingungen suspendiert, so war eine deutliche Adsorption im Elektronenmikroskop<sup>11</sup> sichtbar (Abb. 12). Von den Sorptionsstellen der einzelnen Minerale verlaufen die Fäden nach allen Richtungen zu den benachbarten Tonteilchen und verbinden diese miteinander. Das gleiche Verhalten wie Krilium zeigten auch andere Linearkolloide, wie z. b. die Polyuronsäuren, die Shorey und Martin,<sup>12</sup> U. Springer<sup>13</sup> in Böden und W. G. Forsyth<sup>14</sup> in Fulvosäurefraktionen nachgewiesen haben.

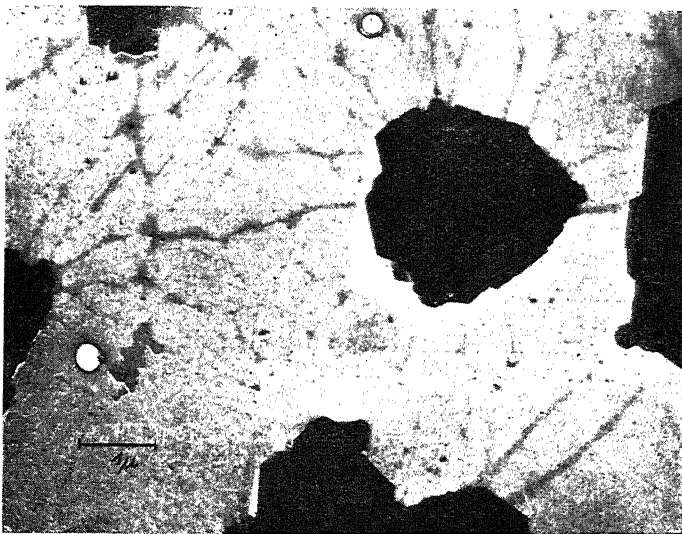


Abb. 12. Kaolinit mit Krilium suspendiert

Auch Metallkolloide, wie das negativ geladene Goldsol, werden von den Kriliumfäden festgehalten. Der Verlauf der Linearkolloide, die teilweise unter der Auflösungsgrenze des Elektronenmikroskops liegen, wird sogar durch Goldteilchen markiert (Abb. 13). Suspendierten wir Kaolinit mit Krilium und blauem Goldsol, so fanden wir eine bevorzugte Adsorption der Goldteilchen an den Kriliumfäden. Dies gab zu der Vermutung Anlass, dass die Kettenmoleküle des Kriliums zu fadenförmigen Gebilden zusammengelagert sind und dabei die Teilchen mechanisch umschlingen und zusammenhalten.

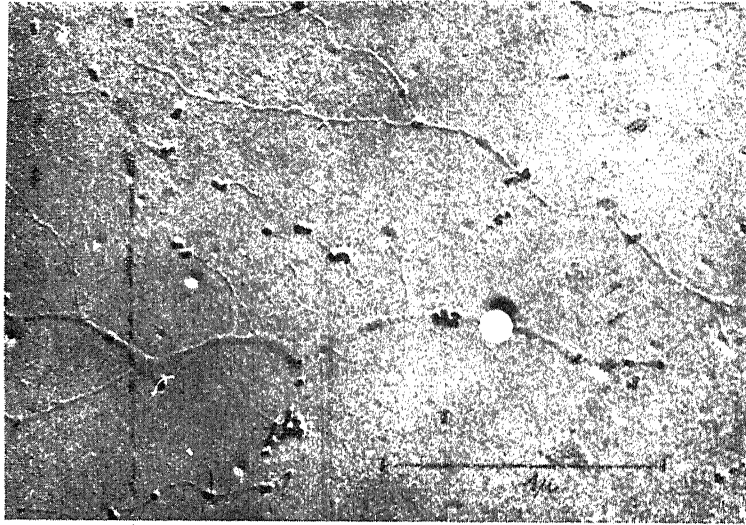


Abb. 13. Goldsol mit Krilium suspendiert

Da man bei der Elektronenmikroskopie die Präparate schonend trocknen muss, könnte man uns hier die gemachten Beobachtungen über die Sorption von Linearkolloiden an Tonmineralen als Trocknungseffekt vorhalten. Um dies zu überprüfen, haben wir Adsorptionsversuche durchgeführt. Da die Linearkolloide sich im Gegensatz zu den Sphärokolloiden durch eine hohe Viskosität auszeichnen konnten wir aus der Viskositätsdifferenz vor und nach der Adsorption die adsorbierte Menge direkt bestimmen. Die Sorptionskapazität ist weitgehend von der Fadenlänge, der Konzentration und der Art des gewählten Tonminerals abhängig.

Mit diesem Kurzreferat bezweckten wir hauptsächlich, auf die Möglichkeiten der Elektronenmikroskopie bei der Erforschung der Wechselwirkung zwischen den anorganischen und organischen Kolloiden im Boden hinzuweisen. Eine ausführlichere Mitteilung über diesen Fragenkomplex wird demnächst von uns veröffentlicht.

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# DER EINFLUSS DES THYMOHYDROCHINONS ALS MODELLSUBSTANZ VON VORSTUFEN BZW. ABBAUPRODUKTEN VON HUMINSÄUREN AUF DIE KEIMUNG VON GETREIDE

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Bereits um 1800 wies Albrecht Thaer auf die Bedeutung des Humus für das Pflanzenwachstum hin und seit dieser Zeit wird versucht, den Humuszustand der Ackerböden möglichst günstig zu gestalten. Die Auswirkungen einer guten Humuswirtschaft sind bekannt. Viel weniger aber weiss man über die Ursachen der Humuswirkung. Von wissenschaftlicher Seite wurde versucht, diese aufzuklären. Vor allem befasste man sich mit den physikalischen Eigenschaften. Es sei nur an Arbeiten über den Einfluss auf den Wasserhaushalt, das Sorptionsvermögen oder die Struktur der Böden erinnert. Die Frage der direkten Einwirkung des Humus auf den Stoffwechsel der Pflanze wurde weitaus weniger untersucht. Die Ergebnisse der einzelnen Autoren stehen z. T. im Widerspruch. Dies ist auch verständlich, denn nach W. Kubiśna<sup>1</sup> bezeichnet man als Humus "die Gesamtheit jener organischen Stoffe eines Bodens, die sich unter den in ihm herrschenden Zersetzungsbedingungen als schwer zersetzbar erwiesen haben und darum in charakteristischer Weise zur Anhäufung gelangt sind."

Die verschiedenen Versuchsansteller haben zwar alle mit einer bestimmten Humusfraktion gearbeitet, in dieser aber die unterschiedlichsten Substanzen gehabt. Aus diesem Grunde führten wir unsere Untersuchungen über den Einfluss der Humusstoffe auf die Keimung von Getreide mit einer Modellschubstanz durch. Wir wählten das Thymohydrochinon, das auf Grund seiner chemischen und physikalischen Eigenschaften als Modell von Vorstufen bzw. Abbauprodukten von Huminsäuren angesehen werden kann.

Als Versuchspflanzen wurden

1. Heines Peko Sommerweizen.
2. Petkuser Sommerroggen.
3. Heines Heisa II Sommergerste.
4. Petkuser Hafer Flämingsgold.

verwendet. Zunächst sollte festgestellt werden, ob durch wässrige Thymohydrochinonlösungen die Keimgeschwindigkeit der vier genannten Getreidearten beeinflusst wird. Dabei bedienten wir uns der folgenden Methode:

100 Getreidekörner wurden in eine Petrischale gegeben, die zwei Blatt Filtrierpapier enthielt, das mit 5 c.cm der zu prüfenden Lösung befeuchtet war. Die Körner

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\* Anschrift: Braunschweig, Bundesallee 50.

wurden mit einem Blatt Filtrierpapier bedeckt, auf das 2 c.cm der Lösung gegeben waren. Die Schalen wurden bei 27°C im Brutschrank aufgestellt. Die erste Auszählung der gekeimten Körner erfolgte bei Weizen, Roggen und Gerste nach 16 Stunden, bei Hafer nach 40 Stunden. Das Thymohydrochinon wurde als 0,025, 0,0025, 0,00025, und 0,000025% ige wässrige Lösung geprüft

Aus der Abb. 1. sind die mit Weizen erzielten Versuchsergebnisse zu entnehmen.

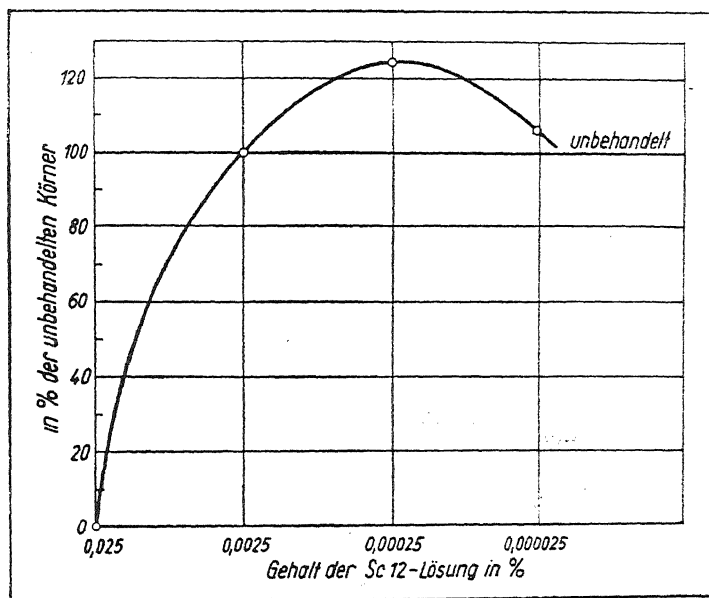


Abb. 1.—Beeinflussung der Keimgeschwindigkeit von Weizen durch Thymohydrochinon  
(= Sc 12)

Bei den in 0,025% iger Thymohydrochinonlösung angesetzten Körnern unterblieb die Keimung völlig. Die 0,0025% ige Lösung hatte keinen Einfluss auf die Keimgeschwindigkeit. Eine Erhöhung um 23% wurde durch die 0,00025% ige Lösung erzielt. Eine weitere Verminderung der Thymohydrochinonkonzentration liess die Förderwirkung wieder absinken.

Die Versuche mit den anderen Getreidearten führten zu ähnlichen Ergebnissen. Die Keimgeschwindigkeit des Roggens wurde ebenfalls durch die 0,00025% ige Lösung am stärksten beschleunigt. Bei Gerste dagegen wirkte die 0,000025% ige Lösung optimal. Hafer scheint schwächer als Weizen auf Thymohydrochinon zu reagieren, denn die 0,025% ige Lösung verminderte die Keimgeschwindigkeit nur um 40% während sie bei Weizen zur totalen Keimhemmung führte. Optimal wirkte bei dieser Getreideart die 0,0025% ige Lösung. Durch sie wurde die Keimgeschwindigkeit um 15% erhöht.

Durch wässrige Thymohydrochinonlösungen liess sich also die Keimgeschwindigkeit von Weizen, Roggen, Gerste und Hafer erhöhen. Gleiche Thymohydrochinonkonzentrationen hatten dabei auf die verschiedenen Getreidearten einen

unterschiedlichen Einfluss. Zur Stimulierung der Keimung der Gerste scheinen geringere Substanzmengen nötig zu sein, als zu derjenigen der übrigen Getreidearten.

Um die Ursachen dieser Förderwirkungen kennenzulernen, untersuchten wir den Einfluss auf verschiedene Stoffwechselvorgänge. Es wurde zu diesen Arbeiten nur Weizen der bereits genannten Sorte verwendet.

Als erstes wurde eine Erhöhung der Wasseraufnahme keimender Körner durch Thymohydrochinon gefunden. Da nach L. Henderson<sup>2</sup> und C. H. Bailey<sup>3</sup> ein enger Zusammenhang zwischen Wasseraufnahme und Atmung besteht, bestimmten wir die  $\text{CO}_2$ -Ausscheidung der keimenden Körner mittels einer von uns an anderer Stelle beschriebenen Methode<sup>4</sup> und der Methode von <sup>1</sup> Kappen, J. Hofer, E. Grosse-Braukmann<sup>5</sup> und fanden eine Erhöhung um 35 bzw. 38% durch die 0,00025% ige Thymohydrochinonlösung. Die Ergebnisse beider Methoden stimmten somit gut überein. Es lag der Gedanke nahe, dass eine Beeinflussung der Atmung die Ursache der Förderung der Keimgeschwindigkeit ist.

Die Atmung der Pflanze kann man in drei Abschnitte teilen. Im ersten findet der Abbau der Kohlenhydrate zu Brenztraubensäure statt; den zweiten bildet die Oxydation der Brenztraubensäure, nach dem Cyklus von H. A. Krebs und W. A. Johnson<sup>6</sup>. Im letzten erfolgte die Bindung des von den Dehydrasen abgespaltenen Substratwasserstoffes mit Luftsauerstoff zu Wasser. Die einzelnen Prozesse verlaufen in der Hauptsache durch Phosphorylierungen und Dehydrierungen.

Aus den Untersuchungen von W. Langenbeck<sup>7</sup> ist nun bekannt, dass Chinone als Modelle von Dehydrasen bei der oxydativen Desaminierung von Aminosäuren auftreten können. Es musste deshalb untersucht werden, ob das Thymohydrochinon gleiche Eigenschaften aufweist und dadurch eventuell einen Einfluss auf die dehydrierenden Vorgänge bei der Atmung besitzt. Mit Hilfe einer an anderer Stelle beschriebenen Methode<sup>4</sup> gelang es sowohl Glykokoll als auch Natriumcitrat zu dehydrieren. W. Flaig und K. Reinemund<sup>8</sup> untersuchten dieses Problem näher und konnten weitere Einblicke in diesen Wirkungsmechanismus finden.

W. Langenbeck<sup>7</sup> führte seine Untersuchungen z. T. mit Isatin als Dehydrasemodell durch. Wenn nun die Eigenschaft Wasserstoff zu übertragen die Ursache der Keimbeschleunigung durch Thymohydrochinon ist, dann müsste auch durch Isatin diese erhöht werden können. Wir prüften diese Frage nach und fanden tatsächlich eine Förderung.

Wie bereits erwähnt, spielen dehydrierende Vorgänge bei der Atmung und besonders im "Krebszyklus" eine grosse Rolle. Durch Blockierung bestimmter Dehydrasen sollte festgestellt werden, an welcher Stelle das Thymohydrochinon in den Atmungsprozess eingreift. Nach B. Commoner und K. V. Thimann<sup>9</sup> wird sowohl die Malonsäuredehydrase als auch Triosephosphatdehydrase durch Monojodessigsäure gehemmt. Wir verwendeten zunächst diese Substanz. Die durch sie hervorgerufenen Hemmungen liessen sich durch Thymohydrochinon zum grossen Teil wieder aufheben. Auch Hemmungen durch Malachitgrün oder Malonsäure, die ein spezifischer Hemmstoff der Bernsteinsäuredehydrase sein soll, konnten durch Thymohydrochinon ausgeglichen werden. Auf Grund dieser Befunde glauben wir an keine direkte Beeinflussung der im Atmungszyklus wirkenden Substratdehydrasen. Wir befassten uns deshalb mit den Vorgängen der Endoxydation, in dem der vom Substrat abgespaltene Wasserstoff mit Luftsauerstoff zu Wasser reagiert.

Nach den Untersuchungen von J. A. Boswell und G. C. Whiting<sup>10</sup> spielen dabei die Polyphenoloxidasen eine Rolle. Es wurde daher geprüft, ob auch eine Hemmung dieser Enzyme durch Thymohydrochinon wieder aufgehoben werden kann. Wir verwendeten dazu p-Nitrophenol, das nach D. Baker und J. M. Nelson<sup>11</sup> ein spezifischer Hemmstoff der Polyphenoloxidasen sein soll. Die durch diese Substanz hervorgerufene Keimhemmung liess sich mit Thymohydrochinon nicht wieder aufheben. Bei Anwendung der sonst optimal wirkenden Thymohydrochinonkonzentration wurde sie sogar verstärkt. Auf Grund dieses Befundes nehmen wir an, dass Thymohydrochinon zwischen Substratdehydrierung und der letzten Stufe der Endoxydation in den Atmungsstoffwechsel eingreift.

D. Baker und J. M. Nelson<sup>11</sup> stellten bei ihren Untersuchungen fest, dass die Protocatechusaure im Endoxydasesystem der Kartoffel eine Überträgerrolle spielt. Da wir das gleiche von Thymohydrochinon bei Weizen annehmen, prüften wir die Beeinflussung der Keimung des Weizens durch diese Substanz. Sie beschleunigte ebenfalls diesen Prozess. Da das erste Oxydationsprodukt der Protocatechusaure wegen der Tautomerie der o- und p-Oxychinone eine gewisse Ähnlichkeit mit dem ersten Oxydationsprodukt des Thymohydrochinons besitzt, und auf Grund der von uns gefundenen Versuchsergebnisse, schreiben wir dem Thymohydrochinon gleichfalls eine Überträgerrolle im Endoxydasesystem zu. Wir sehen dies als eine Ursache der Beschleunigung der Keimgeschwindigkeit an, denn durch eine raschere Reoxydation der Substratdehydrasen können die dehydrierenden Vorgänge der Atmung schneller verlaufen und diese somit intensiver vonstatten gehen. Unter Zugrundelegung dieser Annahme können alle gefundenen Versuchsergebnisse erklärt werden.

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# THE CLAY FRACTIONS OF SOME LIMESTONE SOILS OF THE REMBANG HILLS AND MADURA (INDONESIA)

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## INTRODUCTION

Different kinds of clay minerals are found in soils derived from limestones, e.g., Endell noticed in limestone soils of Europe illite, kaolinite, metahalloysite, montmorillonite and in limestone soils from the Mediterranean region metahalloysite and illite. Schaufelberger<sup>10</sup> found in rendzina soils of Columbia kaolinite, goethite, gibbsite and quartz. Hardon and Favejee<sup>5</sup> established montmorillonite, metahalloysite and kaolinite in limestone soils in middle and east Java and Hardon<sup>6</sup> found metahalloysite.

This divergence in results is not very surprising because the climatic conditions, under which these limestone soils are formed, may be very different. Therefore, in this paper, some other limestone soils from Indonesia were investigated with respect to their clay minerals. The question of the weathering sequence will be discussed in another paper.

## MATERIALS AND METHODS

The following profiles of the Rembang hills were examined: red limestone soils, dark brown limestone soils, black limestone soils, and yellow limestone soils. Of Madura: grey-brown limestone soils, brownish black limestone soils and a black marginalitic soil.

The samples were fractionated in the usual way; the fractions  $< \frac{1}{2} \mu$  from the red soils were treated for removal of the free iron oxides by sodium dithionate according to Deb<sup>2</sup>. The fractions, thus obtained were used for X-ray analysis. X-ray equipment consisted of a Phillips X-ray apparatus fitted with a copper-target X-ray tube and nickel filter.

The profile descriptions are as follows:—

### REMBANG HILLS

Red limestone soils  
58418 0-10 cm

Profile 1, No. 58418/20, altitude  $\pm 101$  m.  
Reddish brown, pseudo sandy, crumbly top-layer  
with many roots; moderate contraction joints when  
drying.  
Colour Munsell 5YR 4/3.

58419	10-30cm	Brownish, weakly red-brown spotted layer, with a few roots. Colour Munsell 5YR 4/6.
58420	30-?cm	Red-brown layer with iron spots and many small white spots ; a very few roots. Colour Munsell 5YR 4/4.
Profile 2, No. 58519/20		Altitude $\pm$ 220 m
58519	0-15 cm	Brownish, some what sandy top-layer with a few roots. Colour Munsell 5YR 3/4.
58520	15-? cm	Red-brown, somewhat clayey, plastic layer with some roots. Colour Munsell 2.5YR 3/6.
Profile 3, No. 61054/56		Altitude $\pm$ 150 m
61054	0-13 cm	Brown, pseudo sandy, dusty top-layer, with many roots. Color Munsell 5 YR 3/4.
61055	13-35 cm	Brown, somewhat sandy, sticky layer with still many roots. Colour 5YR 4/6.
61056	35-60 cm	Brown, somewhat sandy, rather strong, sticky sub-layer ; no roots. Colour 5YR 4/4.
Dark brown limestone soils		Profile, 4, No. 58380/81, altitude $\pm$ 100 m.
58380	0-5 cm	Grey-brown, sandy top-layer with many limestone concretions and many roots. Colour 5YR 4/2.
58381	5-25 cm	Light brown dusty-sandy layer with very many limestone concretion ; a few roots. Colour 5YR 4/4.
Profile 5, No. 58368/69		Altitude $\pm$ 150 m.
58368	0-10 cm	Dark brown, somewhat plastic, fine sandy top-layer with many roots. Colour 7.5YR 3/2.
58369	10-30cm	Dark brown, somewhat plastic sub-layer with some coarse limestone concretions ; somewhat sandy and no roots. Colour 5YR 4/2.
Profile 6, No. 60393		Altitude $\pm$ 250 m.
		Dark brown, crumbly top-soil with moderate contraction joints ; not very sticky and plastic, forms pseudo sand when dry ; perforated by crystalline limestone, contains some iron concretions. Colour 7.5YR 3/2.
Black limestone soils,		Two surface soil samples were taken, one at 290 m altitude and the other at 200 m altitude. The description of both samples is as follows :—
Profile 7 and 8, No. 60659 and 60696 resp.		Alt. resp. $\pm$ 290m and $\pm$ 200 m. Brown-black moist soil under thick vegetation cover, crumbly, sticky and plastic ; forms pseudo sand when dry, perforated by crystalline limestone. Colour 10YR 2/2.

Yellow limestone soils	Profile 9, No. 58335/37, altitude $\pm$ 75 m.
58335 0-10 cm	Very dark gray sandy top-soil with some iron concretions, only a few roots. Colour 10YR 3/1.
58336 10-40 cm	Brownish yellow strongly sticky, crumbly sub-soil, with many small iron concretions and a few roots. Colour 10YR 6/6.
58337 40-? cm	Lime containing quartz sandstone.
Profile 10, No. 61112/14	Altitude $\pm$ 225 m.
61112 0-14 cm	Dark brown, rather plastic loose soil, containing organic material with many rock pieces and many roots, crumbly; a few iron concretions. Color 10YR 4/3.
61113 14-28 cm	Dark brown, strongly sticky, less loose soil with less organic material and many rocks. Colour 10YR 4/3.
61114 28-50 cm	Dark yellowish brown, rather compact soil, strongly sticky, with many rocks and few roots, lying sharply on limestone. Colour 10YR 4/4.
Profile 11, No. 61134/36	Altitude $\pm$ 225 m.
61134	Dark yellowish brown plastic, somewhat sandy soil with a few iron concretions and a few roots. Colour 10YR 4/4.
61135	Yellow brown plastic, strongly stricky layer with a few roots. Colour 10 YR 5/4.
61136	Yellow brown, strongly sticky sub-soil with a few small limestone and iron concretions and a few roots. Colour 10YR 5/6.

#### MADURA

Gray brown limestone soil	Profile 12, No. 81242/43, altitude $\pm$ 30 m.
81242 0-20 cm	Dark red brown soil when dry; crumbly but rather cloddy with iron concretions. Color 5YR 3/3. Rapidly changing into.
81243 20-<70 cm	A moist blue gray compact greasy layer with brown spots, rich in brown black iron particles. Colour 7-5YR 6/0.
Black limestone soil	Description of which is as follows :—
Profile 13, No. 81257/58	Altitude $\pm$ 224 cm.
81257 0-15 cm	Moist black crumbly to cloddy, quartz containing soil with many limestone particles, sharp lying on 81258. Colour 10YR 2/2.

81258 15-2 cm White yellow hard crystalline limestone with shells and calcite veins. The limestone penetrates through the soil and has only few holes.

Grey brown to black marginalitic soil. Here also only a surface soil sample was examined.

Profiles 14, No. 84431/32  $\pm$  120 m.

84431 0-15 cm Dry brown grey, cloddy to crumbly top-soil, rich in limestone fragments and limestone lumps, gradually changing into 84432.  
Colour 5YR 4/1.

84432 15-50 cm When moist brownish dark gray, when dry dark gray, cloddy sub-soil, rich in limestone fragments.  
Colour 5YR 4/1 (dry).  
5YR 4/2 (wet).

The clay fractions of all profiles and surface soil samples contain as predominant minerals beidellite or nontronite. It is difficult to distinguish between these minerals because the diffraction lines of both coincide to a great extent (see Hanawalt<sup>4</sup>, and table 1 at the end of this paper). Admixtures are kaolinite, montmorillonite, halloysite,  $\alpha$ -cristobalite and goethite. The percentages of those minerals vary somewhat and in some cases rather strongly. For details see tables 5 to 20 at the end of this paper.

These results are surprising, because Hardon and Favejee<sup>5-6</sup> when examining the soils of the southern limestone zone (Solo zone), found as predominant clay-mineral meta-halloysite. Whether this is the result of climatic influences or of other circumstances has to be investigated in more detail.

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TABLE 1

X-RAY DATA ACCORDING TO HARDON AND FAVEJEE

Sample No.	Residence	Soil description	Clay mineral
9170	Surakarta	Reddish brown limestone soil	methalloysite
19208	Djocjakarta	Idem	methalloysite
27009	Surakarta	blackish brown limostone soil	montmorillonite-metahalloysite (few)—kaolinite (few).
27028	Surakarta	Black limestone soil	metahalloysite

TABLE 2

X-RAY DATA ACCORDING TO ENDELL (IN KUBIENA)

KALKSTEINBRAUNLEHME :

Sch. 18 Terra fusca auf Wettersteinkalk, Trinksteinsattel, Rax	Glimmerartiges tonmineral und kaolinit
G2, Terra fusca auf Hauptdolomit, Grubberg (Nieder-Osterreich) B-Horizont.	Methalloysite, montmorillonit, glimmerartiges Tonmineral, und Kaolinit.
dto, CaC-Horizont.	Glimmerartiges tonmineral, metahalloysit und nicht naher indentifizierbares tonmineral.
151 Terra fusca auf Kalkstein, Wienerwald.	Glimmerartiges tonmineral

KALKSTEINROTHLEHME

Terra rossa, rovigno	Metahalloysit und glimmerartiges tonmineral.
Terra rossa, velca, Albanien	Glimmerartiges tonmineral und metahalloysit.
L1, Terra rossa, adriagebiet (Leinigen)	Metahalloysit

TABLE 3

X-RAY DATA OF BEIDELLITE AND NONTRONITE ACCORDING TO NAGELSCHMIDT  
FROM THE HANAWALT TABLES (A. S. T. M.)

Beidellite of Beidell, Sagnache, Col.		Nontronite of Nontron, Dordogne	
d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
15.2	60	15.4	100
5.05	40	—	—
4.51	100	4.56	100
3.36	40	—	—
—	—	3.11	20
3.03	40	3.03	20
2.60	100	2.64	80
2.54	100	2.56	80
—	—	2.43	40
2.38	40	—	—
2.24	20	—	—
2.14	20	—	—
1.70	60	1.72	40
1.64	100	1.67	40
1.50	100	1.52	100
—	—	1.32	20
1.30	40	1.30	20
1.29	40	—	—
1.25	40	1.26	20

TABLE 4

CHIEF DIFFRACTION LINES OF BEIDELLITE AND NONTRONITE ACCORDING  
TO THE A. S. T. M. TABLES (HANAWALT)

Beidellite	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>
1	15.1	100	4.46	100	3.03	100
2	15.1	100	4.45	100	3.03	100
3	14.6	100	1.49	100	4.36	80
4	4.52	100	2.61	100	2.55	100
5	4.51	100	2.60	100	2.54	100
Nontronite						
1	15.6	100	4.55	100	1.52	100
2	15.4	100	4.56	100	1.52	100
3	14.7	100	4.48	40	1.50	20b
4	13.9	100	4.50	70	1.52	50
5	4.56	100	1.53	100	2.56	90
6	4.51	100	2.54	100	1.49	100
7	13.5	100	1.54	60	4.5	60
8	4.52	100	2.55	100	1.49	100
9	13.9	100	4.44	80	3.54	50
10	12.4	100	4.48	100	1.51	100
11	14.1	100	4.55	40-	1.52	40-
12	7.2	100	3.58	100	2.41	100
13	13.4	100	1.51	60	4.51	40
14	18.8—15.6	100	4.66	80	1.53	60
15	23.1—17.9	100	4.66	80	9.53	60

TABLE 5

Profile 1—Red limestone soils, fraction  $< \frac{1}{2}\mu$ , Cu-target  $K\alpha = 1.5374\text{\AA}$ 

58418		58419		58420		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
		10	10.455	10	10.496	mo
40	7.274					ka
		30	7.024	30	7.061	ka
30	6.705					zeolite?
100	4.562					beidell (nontr)
		100	4.391	100	4.427	beidell
30	4.121					nontr
		20	4.071	40	4.065	$\alpha$ -crist
60	3.604	40	{ 3.561 } { 3.448 }	50	{ 3.604 } { 3.474 }	hall-ka
20	2.731					ka
70	{ 2.629 } { 2.540 }	10	2.632		2.670	metahal
		40	{ 2.535 } { 2.457 }	60	{ 2.563 } { 2.506 }	beidell (nontr-ka- goeth)
25	2.369					beidell-metahal
		15	2.316	20	2.320	metahal
10	2.217	10	2.171	10	2.212	beidell-ka
10	2.032					$\alpha$ -crist
		5	1.957	15	1.75	metahal-ka
5	1.851					$\alpha$ -crist
30	{ 1.733 } { 1.676 }	5 br.	1.665	50	{ 1.708 } { 1.665 }	beidell (nontr-met- ahal)
10	1.556			10	1.548	ka-hall
75	1.514	60br	1.475	70	{ 1.495 } { 1.480 }	metahal
				10	1.443	$\alpha$ -crist
5	1.307	20	1.30	5	1.289	beidell (nontr)-ka
5	1.247	5	1.228	10	1.237	beidell-ka-metahal

Profile 2 —Red limestone soils, fraction  $< \frac{1}{2} \mu$ , Cu-target  $K\alpha = 1.5374 \text{ \AA}$

58519		58520		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
10	10.751			mo
30	8.909			?
		40	7.214	ka
		10	6.790	zeolite ?
100	4.405	100	4.449	beidell (nontr)
		10	4.127	nontr (ka-goeth)
70	4.0.1			$\alpha$ -crist
60	3.538	40	3.547	hal-ka
10	3.123			$\alpha$ -crist
		10	2.704	ka
10	2.657			metahal
70	{ 2.559 }	40	{ 2.595 }	beidel (nontr-ka-
	{ 2.468 }		{ 2.517 }	goeth)
				$\alpha$ -crist
30	2.328	10	2.351	beidell metahal-ka
15	2.193	5	2.216	beidell-ka
10	1.977			ka
40br	1.683	23	1.702	beidell(nontr-metahal)
80	1.484	80	1.511	beidell-nontr-ka
10	1.283	10	1.292	beidell-nontr-ka
20	1.231	10	1.241	beidell-ka-metahal

TABLE 7

Profile 3—Red limestone soils, fraction  $< \frac{1}{2} \mu$ , Cu-target  $K\alpha = 1.5374 \text{ \AA}$

61.054		61.055		61.056		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
		40	7.156	10	11.650	mo
		10	6.589			ka
20	6.589			25	6.655	zeolite ?
100	4.341	100	4.441	100	4.391	beidell.
					4.090	goeth.
10	4.032	10	4.011			$\alpha$ -crist.
10	3.483	20	3.524	15	3.488	hal-ka
		10	3.170			$\alpha$ -crist
		60	{ 2.566 }			
40	2.499		{ 2.479 }	70	2.510	beidell (nontr-ka-goeth)
30	2.437			20	2.488	nontr
		20	2.324	10	2.371	beidell-metahal-ka
35	2.280			10	2.271	beidell
		5	2.197			beidell
		8	2.003			$\alpha$ -crist
		8	1.965			ka
10br	1.659	25	{ 1.705 }	20	1.668	beidell (nontra-metahal)
			{ 1.646 }		1.606	ka- $\alpha$ crist
		50	1.501	15	1.511	beidell (nontr)
60	1.455		1.478			beidell (nontr)
			1.292	80	1.459	beidell-ka
		8	1.250	20	1.281	beidell (nontr)-ka
		8				beidell (nontr)
20	1.215			10	1.220	beidell-ka-metahal.



TABLE 8

Profile 4—Dark brown limestone soils, fraction $< \frac{1}{2}\mu$ , Cu-target $K\alpha = 1.5374 \text{ \AA}$				
58380		58381		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
		10	13.025	mo
		10	11.753	mo
		5	7.499	metahal
5	5.700			?
		5	4.728	gibbs
100	4.456	100	4.472	beidell-gibbs
200	4.109	30	4.090	$\alpha$ -crist
		10	3.585	hal-ka
20	3.501			hal-ka
5	3.341			qu. ?
80	2.575			
20	2.497	75	{ 2.587 } { 2.524 }	beidell
10	2.301	5	2.336	beidell-metahal
20	1.970			$\alpha$ -crist ?
25br	1.686	30	{ 1.723 } { 1.648 }	beidell- $\alpha$ -crist
75	{ 1.501 } { 1.487 }	80	{ 1.506 } { 1.486 }	beidell-metahal-calc
5	1.447			$\alpha$ -crist
10	1.346	5	1.369	$\alpha$ -crist-calc
8	1.288	10	1.293	beidell-nontr
5	1.241	5	1.238	beidell-ka-metahal-calc

TABLE 9

Profile 5—Dark brown limestone soils, fraction $< \frac{1}{2}\mu$ , Cu-target $K\alpha = 1.5374 \text{ \AA}$				
58368		58369		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
indist	11.159	indist.	20.978	mo
20	7.293	30	7.155	mo
100	4.547	100	4.419	ka
20	4.252	30	4.205	beidell
25	3.608	40	3.528	ka
10	3.174			(metahal)-ka
60	2.595	60	2.535	$\alpha$ -crist
		10	2.479	beidell-calc
10	2.450	10	2.406	beidell-calc- $\alpha$ -crist
25	2.349	40	2.314	ka (metahal)
10	2.242	10	2.181	calc $\alpha$ -crist
		10	1.969	beidell
				$\alpha$ crist ?
20	{ 1.734 } { 1.663 }	30	{ 1.699 } { 1.631 }	beidell $\alpha$ -calc
	1.506	70	1.480	beidell-calc
70	1.299	10	1.279	beidell-calc
10	1.253			beidell-ka
12		15	1.227	ka

TABLE 10

Profile 6—Dark brown limestone soils, fraction  $< \frac{1}{2} \mu$  Cu-target  $K\alpha = 1.5374 \text{ \AA}$

60393	I/I <sub>1</sub>	d	Mineral
	100	4.456	beidell-metahal
	80	4.035	a-crist
	5	3.561	metahal
	5	3.297	beidell
	50	2.563	beidell
	30	2.483	beidell-calc-a-crist
	30 br	1.685	beidell-a-crist
	60 br	1.492	beidell-calc-a-crist

TABLE 11

Profiles 7 and 8—Black limestone soils, fraction  $< \frac{1}{2} \mu$ , Cu-target  $K\alpha = 1.5374 \text{ \AA}$

60659	I/I <sub>1</sub>	d	60696	I/I <sub>1</sub>	d	Mineral
				15	10.135	mo
				20	6.987	ka
				10	6.293	?
				15	4.791	a-crist
						gibbs
100	4.524					beidell
				75	4.434	beidell-metahal
20	4.258					a-crist
				100	4.011	a-crist
40	3.613					metahal
				20	3.515	ka
10	3.430					ka
				20	3.297	qu ?
				30	3.126	a crist
				25	2.967	ca ?
				30	2.835	a-crist
				5	2.654	metahal
60	2.587			40	2.554	beidell-metahal-ka
				50	2.476	a-crist
10	2.371			10	2.334	beidell-ka-metahal
				10	2.099	beidell
5	1.981			10	2.007	ka
20	1.937			10	1.921	a-crist
				10	1.858	a-crist
10br	1.706			5	1.718	metahal
				10	1.688	metahal
				5	1.659	ka
				30	1.602	a-crist
50	1.514			5	1.526	a-crist
				45	{ 1.495 }	beidell-ka-metahal
					{ 1.479 }	
				10	1.418	a-crist
				10	1.361	a crist
				15	1.275	a-crist-metahal
				10 br	1.231	a crist-metahal
				10	1.170	a-crist

TABLE 12

Mineral assemblage of the total sand fraction in the fraction III (500-250 $\mu$ ), IV (250-100 $\mu$ ) and V (100-50 $\mu$ ), showing the difference in plagioclase content in the Profiles 7 and 8.

No.	Fraction *	Opaque	Quartz turbid	Quartz clear	SiO <sub>2</sub> org.	Volcanic glass	Orthoclase	Plagioclase	Calcite	Augite	Hypersthene	Gr. amphibole	Br. Gr. amphibole	Bas. amphibole	Zircon	Tourmaline	Apatite
60659	III	1	94	1	1	...	2	tr	1	...	tr	tr	...	...	...	...	...
	IV	1	90	3	...	...	tr	5	...	...	1	...	...	...	...	tr	...
	V	4	85	5	1	...	1	3	...	tr	tr	1	tr	...	tr	tr	...
60696	IV	2	56	3	...	3	tr	32	...	2	2	...	...	tr	...	...	...
	V	1	77	3	1	2	4	10	...	...	1	tr	tr	...	1	...	tr

\* III = 500-250  $\mu$ ; IV = 250-100 $\mu$ ; V = 100-50 $\mu$ .

TABLE 13

Heavy mineral percentage of the Profiles 7 and 8, showing no essential difference

Sample	Opaque	Zircon	Tourmaline	Rutile	Anatase	Augite	Hypersthene	Gr. amphibole	Br. Gr. amphibole	Bas. amphibole	Olivine	Epidote	Apatite
60659	72	14	4	2	...	...	38	38	1	...	1	2	tr
60696	57	12	...	...	tr	2	38	42	3	tr	...	3	...

TABLE 14

Profile 9—Yellow loamy limestone soils, fraction  $< \frac{1}{2} \mu$ , Cu-target,  $K\alpha = 1.5374 \text{ \AA}$ 

58335		58336		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
		20	7.254	ka
100	{ 4.516 }	100	{ 4.602 }	beidell-ka
	{ 4.369 }		{ 4.412 }	
10	4.090	25	4.212	$\alpha$ -crist
				$\alpha$ -crist
60	2.563	30	3.604	metahal
10	2.334	60	{ 2.627 }	beidell
			{ 2.566 }	
		15	2.387	beidell-ka-metahal
		20	1.950	$\alpha$ -crist
30br	1.685	30	{ 1.725 }	beidell-metahal
			{ 1.663 }	
60br	{ 1.504 }	60	{ 1.527 }	beidell
	{ 1.485 }		{ 1.500 }	
5	1.309			beidell

TABLE 15

Profile 10—Yellow loamy limestone soils, fraction  $< \frac{1}{2} \mu$ , Cu-target,  $K\alpha = 1.5374 \text{ \AA}$ 

61112		61113		61114		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
10	10.213					mo
		10	9.415			mo
35	7.214	20	6.987	20	7.042	ka
10	4.817					gibbs
100	4.434	100	4.479	100	4.501	beidell
30	4.102	10	4.115	35	4.166	$\alpha$ -crist
40	3.575	20 br	3.528	20	3.604	ka-metahal
5	3.285					beidell
8	2.667					metahal
60	{ 2.580 }	60	2.552	60	2.587	beidell-metahal
	{ 2.533 }					ka
10	2.420	10	2.423			beidell-ka-metahal
15	2.332	25	2.324	10	2.339	beidell-ka-metahal
5	2.195					beidell
2	2.009			20		beidell
					1.939	$\alpha$ -crist
30	{ 1.709 }	30	{ 1.711 }	20	{ 1.722 }	metahal-beidell
	{ 1.636 }		{ 1.641 }		{ 1.642 }	
		10	1.548			ka
60	{ 1.498 }	60	1.490	50	{ 1.508 }	beidell
	{ 1.485 }				{ 1.495 }	
10	1.287	10	1.284			beidell
10	1.234	10	1.234			$\alpha$ -crist-metahal

TABLE 16

Profile 11—Yellow loamy limestone soils, fraction  $< \frac{1}{2}\mu$ , Cu-target,  $Ka = 1.5374 \text{ \AA}$ 

61134		61135		61136		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
10	10.455			10	7.334	mo
						ka-metahal
10	6.790					zeolite ?
5	4.757					beidell
100	4.369	100	4.427	100	4.524	beidell
10	4.065	5	4.077	30	4.166	a-crist
				5	3.628	metahal
15	3.474			5	3.404	mu
						beidell-ka
5	3.242					mu
50	2.510	50	2.552	70	2.604	beidell-metahal
10	2.371	15	2.425	25	2.461	beidell-ka-metahal
10	2.299			10	2.371	beidell-ka-metahal
				5	1.937	a-crist
10	{ 1.680 }	20	{ 1.703 }	25	{ 1.737 }	metahal-beidell
	{ 1.614 }		{ 1.630 }		{ 1.660 }	
60	{ 1.476 }	60	1.487	60	{ 1.523 }	beidell
	{ 1.459 }				{ 1.504 }	
5	1.275			10	1.308	beidell
5	1.226			10	1.257	a-crist-metahal

TABLE 17

Comparison of the investigated soils of Madura (Profiles 12-14)

81242		81243		81257		77476		84431		Mineral
I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	I/I <sub>1</sub>	d	
40	7.137	30	7.195					20	7.118	ka
								5	4.723	gibbs
100	4.464	100	{ 4.524 }	100	4.449	100	4.449	100	4.539	beidell-metahal
			{ 4.362 }							
15	4.225							10	4.205	ka
50	3.528	40	{ 3.585 }	5	3.506	5	3.539	15	3.515	ka-metahal
			{ 3.501 }					5	3.321	beidell-ka
5	3.375							5	3.077	beidell-ka
										beidell
5	2.634									
60	2.559	50	2.563	60	{ 2.583 }	60	{ 2.578 }	60	2.559	beidell-metahal
					{ 2.506 }		{ 2.521 }			
10	2.476									beidell-a-crist
10	2.425							10	2.410	gibbs
20	2.309	20	2.332	5	2.312	10	2.334	10	2.326	ka
5	2.193									gibbs
				5	2.045					metahal
5	1.978							5	1.961	ka
								15	1.910	ka
15	{ 1.706 }	15	{ 1.701 }	20	{ 1.700 }	20	{ 1.710 }	20	1.693	beidell-metahal
	{ 1.646 }		{ 1.663 }		{ 1.638 }		{ 1.646 }		1.636	
75	{ 1.493 }	60	{ 1.498 }	60	{ 1.506 }	60	{ 1.502 }	70	{ 1.494 }	beidell-ka
	{ 1.476 }		{ 1.484 }		{ 1.484 }		{ 1.485 }		{ 1.478 }	
5	1.290	10	1.284	10	1.293	10	1.287	10	1.284	beidell-ka
5	1.240	8	1.283	10	1.240	10	1.236	10	1.234	beidell-ka-metahal

TABLE 18

Compilation of known X-ray data mentioned in this paper

Sample No.	Origin	Soil type	Mineral									
			Beidellite	Montmorillonite	Kaolinite	Metahalloysite	Quartz	Feldspar	Calcite	$\alpha$ -cristobalite	Gibbsite	Goethite
58418/420	Rembang hills	Red limestone soil	d	tr	m	f	-	-	-	f	-	?
58519/520	"	Idem	d	tr	f	tr	-	-	-	m	-	?
61054/056	"	Idem	d	tr	m	?	-	-	-	f	-	?
58380/381	"	Dark brown lime-stone soil.	d	tr	?	tr	?	-	tr	f	tr	-
58368/369	"	Idem	d	tr	f	f	-	-	tr	tr	?	-
60393	"	Idem	d	-	-	f	-	-	tr	m	-	-
60659	"	Black limestone soil.	d	-	f	m	-	-	-	f	-	-
60696	"	Idem	m	tr	tr	tr	-	-	?	d	tr	-
58335/336	"	Yellow loamy lime-stone soil.	d	-	tr	tr	-	-	-	f	-	-
61112/114	"	Idem	d	tr	f	tr	-	-	-	f	?	-
61134/136	"	Idem	d	tr	tr	tr	-	-	-	f	-	?
30277H	Res. Japara-Rembang (Blora).	Grey old quartz marl soil.	d	f	?	tr	-	tr	-	-	-	-
11863H	Res. Pekalongan.	Yellow young limestone marl soil.	d	f	?	-	-	?	-	-	-	-
12853H	Res. Madiun (Ngawi).	Black old tuff marl soil.	d	-	-	-	-	-	-	-	-	-
12461/523 H	Res. Surakarta	Black old limestone marl soil.	d	f	?	-	-	?	-	-	-	-
33193H	Idem	Idem	d	f	?	-	-	?	-	-	-	-
9170H	Res. Surakarta	Brown red limestone soil.	d	-	-	-	-	-	-	-	-	-
19208H	Res. Djocjakarta.	Idem	d	-	-	-	-	-	-	-	-	-
27009H	Res. Surakarta	Brown black limestone soil.	d	?	f	-	-	-	-	-	-	-
27028H	Res. Surakarta	Black limestone soil.	d	-	-	-	-	-	-	-	-	-
81242/243	Madura	Grey brown limestone soil.	d	-	m	tr	-	-	-	?	-	-
81257	Idem	Brown black to black limestone soil.	d	-	tr	tr	-	-	-	-	-	-
77476	Idem	Idem	d	-	tr	tr	-	-	-	-	-	-
84431	Idem	Grey brown to black margalite soil.	d	-	f	tr	-	-	-	-	tr	-
18A-C Sch.	Quipile, Colombia.	Rendzina	m	d	-	f	-	-	-	f	tr	-

d — dominant.  
m — moderate.f — few.  
tr — trace.? — not certain.  
H — Hardon.

Sch — Schaufelberger.

TABLE 19

Grainsize analyses of the examined soils profiles of the Rembanghills and Madura

Sample No.	Gravel	Fraction									
		I	II	III	IV	V	VI	VII	VIII	IX	X
58418	0.08	0.27	0.92	23.38	13.97	22.33	7.90	8.29	6.39	7.73	8.67
419	0.04	0.26	0.95	9.91	18.94	15.33	5.79	7.52	7.21	11.59	22.16
420	2.5	1.43	1.12	18.31	8.30	11.38	4.27	5.96	6.70	11.77	31.10
58519	0.06	0.32	0.49	1.43	14.74	32.35	11.49	9.68	9.73	9.44	10.88
520	0.1	0.17	0.14	0.25	9.92	22.45	6.56	7.08	8.91	13.90	30.93
61054	—	0.10	0.37	4.72	8.94	25.40	11.01	11.59	11.94	13.12	13.16
055	0.04	0.20	0.36	3.94	6.78	21.21	6.47	9.97	14.07	15.70	21.60
056	0.04	0.21	0.35	2.28	6.29	17.68	5.10	8.75	13.62	19.97	25.87
58380	0.7	0.40	0.93	1.68	4.54	23.34	14.30	16.04	14.22	14.73	9.60
381	5.5	0.47	0.77	1.24	4.47	24.46	14.28	15.89	13.73	15.28	9.94
58368	0.2	0.33	0.50	1.44	4.62	26.29	10.05	12.07	11.21	14.39	19.31
369	2.2	0.40	0.26	1.80	2.02	9.38	5.20	13.32	18.41	22.03	27.70
60393	0.2	0.33	2.56	9.58	11.17	16.29	9.45	16.78	13.71	10.92	9.32
60659	0.4	0.22	1.13	2.19	6.22	24.38	10.63	12.81	14.42	15.02	13.44
60.96	0.3	0.34	2.24	5.93	3.09	16.08	11.33	14.67	17.21	14.95	13.87
58335	0.2	0.58	2.21	7.52	2.78	27.42	10.53	10.66	11.85	14.81	12.42
336	0.3	0.33	1.95	3.69	1.06	17.24	7.65	13.35	18.38	20.53	16.01
337		No analyses									
61112	0.5	0.53	0.68	1.02	1.81	13.41	10.46	11.85	16.85	19.72	22.86
113	0.03	0.39	0.28	0.81	1.01	12.25	9.49	9.87	16.96	20.50	28.60
114	2.3	0.16	0.32	0.24	0.73	9.80	6.71	9.98	14.96	23.77	33.37
61134	0.03	0.16	0.21	1.92	6.61	25.57	14.94	14.07	11.66	13.51	11.72
135	—	0.11	0.14	0.82	7.20	20.28	10.11	11.88	12.30	19.34	18.40
136	0.7	0.11	0.19	0.64	5.57	18.95	12.63	13.22	15.01	19.56	14.19
81242	0.1	0.13	0.26	1.89	1.48	13.42	22.00	16.06	10.50	15.65	19.36
243	0.9	0.22	0.46	0.79	1.39	11.78	19.44	13.93	11.19	18.37	22.46
81257	3.3	0.10	0.19	5.15	5.59	8.50	11.53	14.31	16.72	26.35	11.56
77476	12.7	1.19	1.10	2.98	2.06	6.98	12.38	18.60	18.83	24.55	12.08
84431	2.5	0.66	0.86	2.99	5.80	15.80	15.16	16.07	16.61	20.52	6.01
432	0.9	0.27	0.37	1.88	8.46	17.28	14.04	14.33	16.47	18.95	7.89
		I	2000-1000 $\mu$			VI	50-20 $\mu$				
		II	1000-500 $\mu$			VII	20-5 $\mu$				
		III	500-250 $\mu$			VIII	5-2 $\mu$				
		IV	250-100 $\mu$			IX	2- $\frac{1}{2}$ $\mu$				
		V	100-50 $\mu$			X	< $\frac{1}{2}$ $\mu$				

TABLE 20

Sample No.	Contents of plant nutrition in %						pH	
	P <sub>2</sub> O <sub>5</sub> 25% HCl	2% Citric acid	K <sub>2</sub> O 25% HCl	2% Citric acid	CaO 25% HCl	MgO 25% HCl	H <sub>2</sub> O	KCl
58418	0.026	0.003	0.034	0.019	0.522	0.088	7.3	6.8
419							6.1	4.8
420							6.0	4.8
58519	0.031	0.003	0.026	0.015	0.572	0.091	7.1	6.1
520							6.5	5.0
61054	0.058	0.007	0.020	0.009	0.708	0.084	6.7	5.3
055	0.058	0.005	0.015	0.003	0.678	0.092	6.7	5.3
056							7.2	5.9
58380	0.058	0.007	0.091	0.033	n.d.	0.261	8.2	7.4
381							8.1	7.2
58368	0.050	0.006	0.043	0.016	0.840	0.117	7.0	5.3
369							7.7	7.3
60393	0.097	0.032	0.041	0.024	1.675	0.211	7.9	7.2
60659	0.042	0.008	0.043	0.020	1.156	0.165	7.3	7.1
60696	0.040	0.013	0.109	0.023	2.115	0.225	7.8	6.8
58335	0.084	0.007	0.205	0.026	1.029	0.235	7.4	7.0
336	0.034	0.001	0.100	0.008	1.089	0.301	6.7	5.0
337		No analyses						
61112	0.102	0.010	0.039	0.014	0.936	0.154	7.1	5.4
113	0.059	0.005	0.030	0.011	0.650	0.110	6.0	4.8
114							5.9	4.7
61134	0.022	0.004	0.045	0.008	0.680	0.199	6.4	5.2
135	0.024	0.003	0.038	0.004	0.725	0.234	5.9	4.1
136							7.8	7.1
81242	0.319	0.039	0.050	0.010	0.588	0.127	6.2	4.8
243	0.149	0.018	0.041	0.013	0.751	0.170	6.7	5.1
81257	0.088	0.074	0.047	0.008	2.185	1.228	7.7	6.6
77476	0.183	0.053	0.041	0.010	4.982	0.210	8.0	7.4
84431	0.038	0.015	0.059	0.010	5.767	0.225	8.2	7.1
432	0.035	0.009	0.051	0.011	2.510	0.296	8.0	7.0



# EFFECT OF SOIL DEVELOPMENT ON CHEMICAL COMPOSITION AND THERMAL CHARACTERISTICS OF CLAY

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## INTRODUCTION

The chemical composition and physical properties of the clay separates determine to a large extent the productivity of soils. On account of large surface area as well as the colloid character, the clay separates of soils have been subject of detailed study in India and abroad. Investigations carried out indicate that the clay minerals are essential electrochemical systems and therefore physical properties of soils can be greatly modified by physico-chemical methods. Accordingly, actual structure of clay minerals has been studied in as great a detail as their physico-chemical reactions. Due to the difficulty in isolating the secondary clay minerals in a pure state from the finer fragments of rock minerals, the necessity for comparing the characteristics of isolated clay samples with pure minerals like kaolinite, montmorillonites, etc., has arisen. The analogous characteristics can hardly be considered to indicate their identity with the reference minerals and therefore, results of such studies can at best be near approximations.

The clay characteristics of the different layers of the soil were found similar by Roy (1950) in the case of black soils of Indore, while they were dissimilar in the case of Delhi soils. From the study of fractionated clays from the soils of drainage catena of southern New York, Martin and Russell (1952) found striking similarity of all clay fractions examined with regard to depth. They have observed that finer fractions of clay minerals contained unidentified iron and alumina oxides as impurities in large excess of illite which is present in all layers of the profile. Martin (1954) observed that the mineral composition of clay separate from three major horizons of brown-forest, brown-podsolic and grey-brown podsollic soils of New York State to be different. In this investigation the particle size was  $1.0\mu$ . Nagelschmidt, Desai and Muir (1940) found, on the other hand, little variation in the mineralogical composition of clay throughout the profile. It appears that both the particle size as well as the depth of occurrence may modify the character of clay in soil samples. The investigations reported in this publication throw some light on this aspect of the study of clay separates.

## METHODS AND MATERIALS

Soil samples were obtained from four layers of a profile in field No. D4 of the experimental farm attached to the main Sugarcane Research Station, U. P. at Shalijahanpur. The air-dry soils were passed through a 2.0 m.m. sieve. The prepared samples were treated with N/5 HCl solution for 24 hours and leached in

a Buchner funnel till free from calcium. The residue was further leached successively with N sodium chloride, distilled water and 40 per cent. alcohol till free of chlorides. The residue was carefully datched from the funnel and transferred to a pint-bottle with distilled water and shaken in an end-over-end shaker for 6 hours. The contents of the bottle were then transferred to wide-mouthed bottles of capacity 2000 c.c. with a few drops of N/5 sodium carbonate to give the suspension a distinctly alkaline reaction to litmus paper. The clay samples were obtained by sedimentation method after setting for 96 hours. Fresh samples from field No. A 4 were treated as above to obtain clay samples of 48 hours.

The suspensions were evaporated to dryness and treated with N/2 HCl till the extract gave acidic reaction. The residue was leached with distilled water and 40 per cent. alcohol till free of chlorides. The residue was dried over calcium chloride in a vacuum desicator and preserved for further study.

The chemical analysis was carried out after fusing the clay samples with sodium carbonate. The fused mass was then treated with hydrochloric acid and A. E. A. methods (Wright 1939) were used for the estimation of silica, alumina and iron.

The clay samples were kept for several days in an atmosphere of 75 per cent. relative humidity. The samples were dried at various temperatures in muffle furnace after taking care to circulate air of constant humidity within the furnace. At each temperature the samples were kept for 2-4 hours until there was no further loss of moisture. The furnace used had the thermostatic attachment and temperature maintained was correct up to  $\pm 5^{\circ}\text{C}$ . The exact temperature within the furnace was recorded by a built-in Pyrometer.

The data on chemical composition and dehydration moistures are given in the present paper. Work on other aspects now in progress will be reported elsewhere.

#### DATA AND DISCUSSION

The results of silicate analysis of the two clay fractions are given in Tables I and II, together with the molecular ratios,  $\text{SiO}_2/\text{R}_2\text{O}_3$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  and  $\text{SiO}_2/\text{Fe}_2\text{O}_3$ .

TABLE I  
Chemical analysis and molar ratios of clay ( $\cdot 50\mu$ )

(Field No. D4)				
Depth	0"-7"	7"-17"	17"-33"	33"-58"
$\text{SiO}_2$ %	39.02	42.48	39.96	39.88
$\text{R}_2\text{O}_3$ %	37.50	34.70	39.60	40.60
$\text{Fe}_2\text{O}_3$ %	12.80	11.64	12.04	12.04
$\text{Al}_2\text{O}_3$ %	24.70	23.06	27.56	28.56
$\text{SiO}_2/\text{R}_2\text{O}_3$	2.08	2.37	1.93	1.87
$\text{SiO}_2/\text{Al}_2\text{O}_3$	2.68	3.13	2.46	2.37
$\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$	0.33	0.32	0.28	0.27
$\text{SiO}_2/\text{Fe}_2\text{O}_3$	8.12	9.80	8.80	8.80

[ Field No. A<sub>1</sub> ]

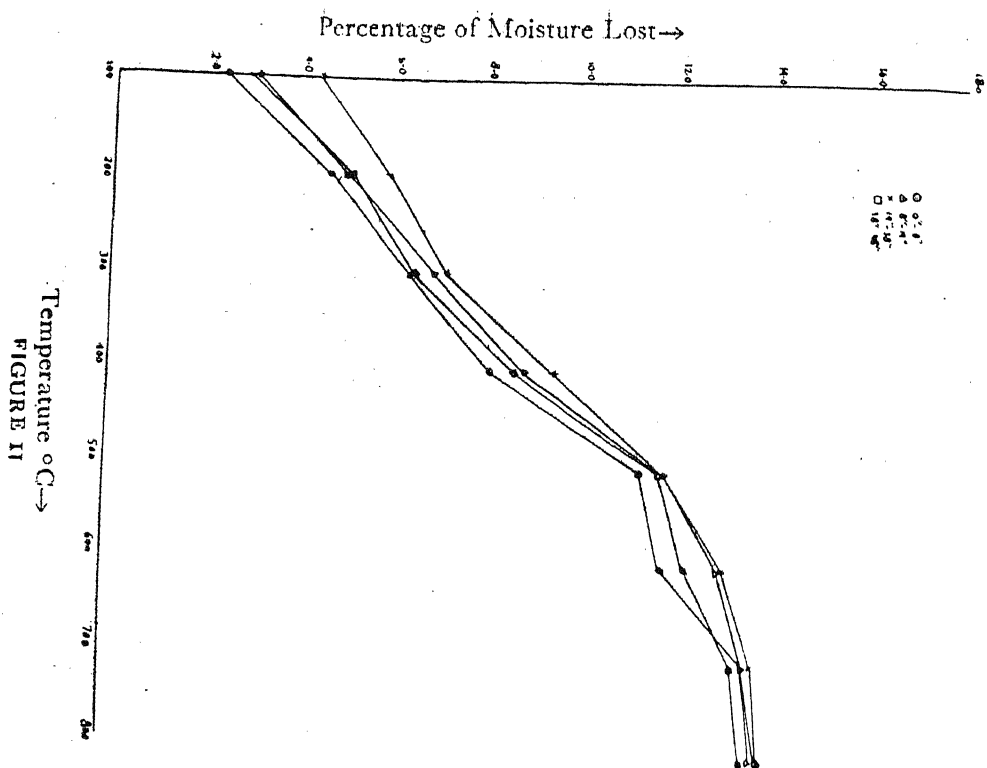


FIGURE II

[ Field No. D<sub>1</sub> ]

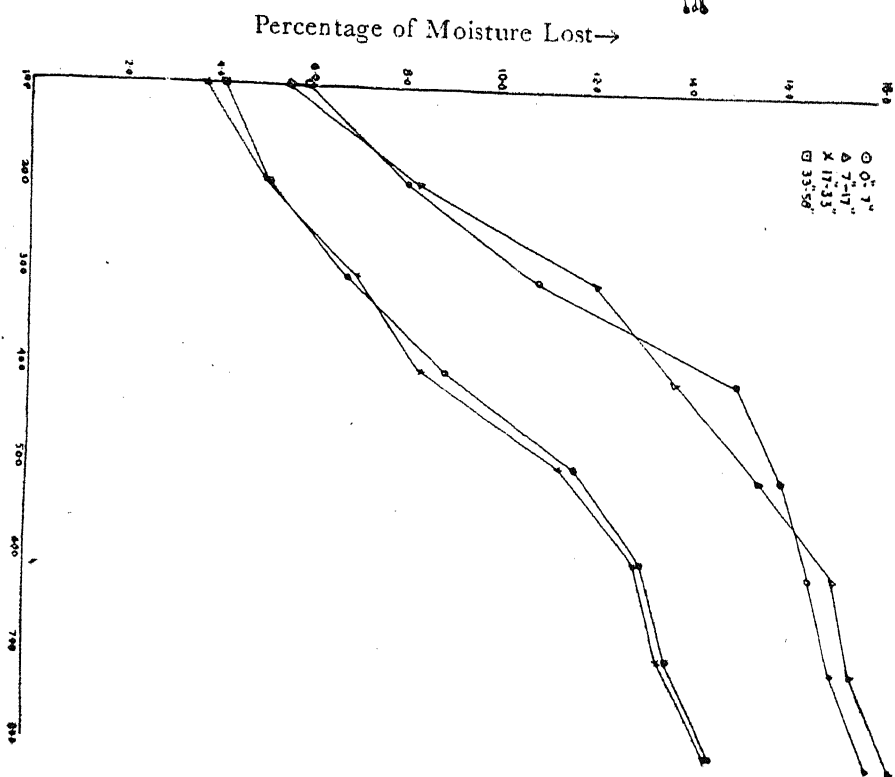


FIGURE I

TABLE II

Chemical analysis and molar ratios of clay ( $\cdot 71\mu$ )

(Field No. A4).

Depths	0"-8"	8"-19"	19"-38"	38"-46"
SiO <sub>2</sub> %	42.92	43.30	43.48	43.30
R <sub>2</sub> O <sub>3</sub> %	39.30	38.00	36.30	37.60
Fe <sub>2</sub> O <sub>3</sub> %	12.00	12.00	12.40	12.80
Al <sub>2</sub> O <sub>3</sub> %	27.30	26.00	23.90	24.80
SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub>	2.08	2.19	2.32	2.24
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2.66	2.83	3.09	2.97
Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.28	0.24	0.29	0.32
SiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	9.53	10.16	10.05	9.14

In the coarser fraction, (Table II) there is no differential eluviation of silica which appears to be constant at all depths of the profile. On the other hand, the total sesquioxide percentages of the horizon of illuviation, namely 17"-38" and 38"-46" are lower than those of the eluvial surface layers. The silica sesquioxide ratios indicate greater accumulation of silica relative to sesquioxides. The iron minerals appear to be richer in the sub-soil than those of alumina. The silica sesquioxides and silica alumina ratios show values intermediate between true montmorillonites and kaolinites. The constancy of SiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> ratios, however, indicates the presence of hydrated mica in these soils, except in the soil layer 38"-46". It is in this layer that iron nodules were observed. From the above it would appear that the clay contains besides secondary clay minerals some hydrated silica and mica and the general tendency of soil forming processes may be comparable to ground water laterites.

On the other hand, the silicate analysis of the finer clay fraction (Table I) gives some what different picture. The illuvial layers between 17"-58" are richer in sesquioxides than the two surface layers. The relatively higher accumulation in this case of sesquioxides is comparable to podsol formation. In this respect alumina appears to be relatively more mobile than iron. As in the previous case silica/iron ratio tends to remain constant at all depths of the solum. The silica sesquioxide ratios tend to be nearer 2.0 while silica alumina ratios indicate characteristic intermediate between montmorillonites and kaolinites. Besides it is also indicated from SiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> ratios that the isolated clay samples contain in addition some quartz and hydrous mica.

It may be observed that there is no difference between the surface layers of the clay separates, while in the case of the coarser fraction the illuvial horizons appear to be more siliceous. This is reflected also by SiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> ratios of the samples. The coarser fraction therefore, contains free quartz of colloidal dimensions besides presumably some hydrous micas, in the sub-soils.

The moisture losses from clay samples at constant humidity on prolonged dehydration at different temperatures are given in Tables III and IV.

[ Field No. D<sub>4</sub> ]

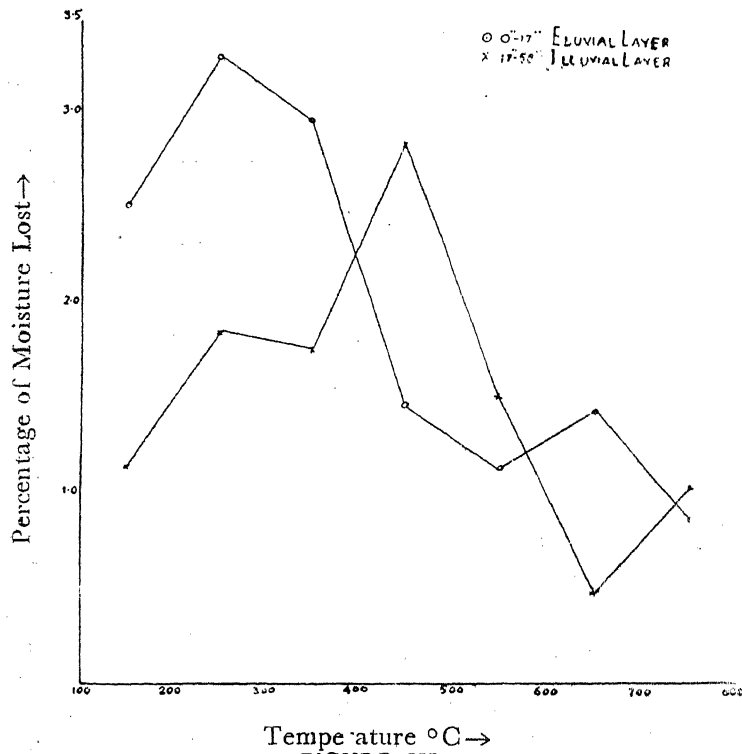


FIGURE III

[ Field No. A<sub>4</sub> ]

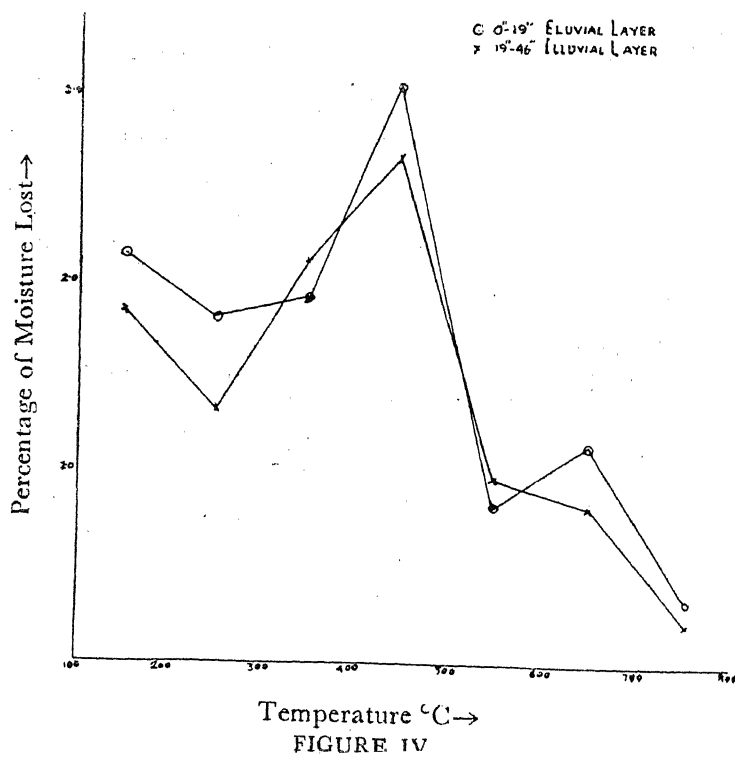


TABLE III

Percentage loss of moisture at different temperatures

(Field No. D4).

Depth.	0"-7"	7"-17"	17"-33"	33"-58"
100°C.	5.95	5.64	3.80	4.19
200°C.	8.24	8.39	5.11	5.20
300°C.	11.01	12.21	7.12	6.88
400°C.	15.22	13.88	8.53	8.96
500°C.	16.22	15.75	11.43	11.71
600°C.	16.85	17.37	12.98	13.15
700°C.	17.13	17.74	13.52	13.68
800°C.	18.15	18.63	14.56	14.69

TABLE IV

Percentage loss of moisture at different temperatures

(Field No. A4).

Depth.	0"-8"	8"-19"	19"-38"	38"-46"
100°C.	2.40	3.08	4.38	3.02
200°C.	4.72	5.10	5.98	5.16
300°C.	6.46	7.04	7.30	6.54
400°C.	8.32	9.06	9.62	8.85
500°C.	11.52	12.00	11.98	11.90
600°C.	12.02	13.18	13.30	12.57
700°C.	13.78	13.78	13.98	13.58
800°C.	14.18	14.02	14.18	13.80

The moisture loss on dehydration at 100°C in the case of the coarser clay fraction is comparatively lower than the finer fraction. The latter may be due to larger surface of adsorption of the finer clay material. This does not, however, appear to be the case in the case of horizons of illuviation, as in both the cases the moisture loss is similar, showing that the loss of moisture is not seriously affected by the available surface area. The nature of thermal dehydration curves of all the four layers of the coarser fraction given in Tables I and II is similar and the depth of sampling of clay appears immaterial in respect to thermal properties of the minerals present. The nature of the curve obtained is similar in pattern to the usual adsorption isotherms up to 300°C and between 300°C and 600°C there is a slight rise in the moisture loss. Beyond 500°C the moisture loss becomes lower. In general the magnitude of loss of moisture is the same between 0-300°C and 300-600°C. In the case of finer fraction on the other hand they are sharply different in features; while the clay samples separated from the horizons of eluviation show characteristic similar to those of the coarser fraction, the horizons of illuviation indicate a loss of moisture between 100°C to 300°C far larger than that obtained by heating the clay fraction up to 600°C. In the case of finer fraction again there is a sharp rise in moisture loss. It would accordingly appear that in the case of alluvial soils the first two layers representing the horizon of eluviation is more weathered than those of the horizon of illuviation.

The average loss of moisture at different temperatures from clay separates of horizons of eluviation and illuviation is given in Tables III and IV, from which it may be seen that the maximum loss of moisture in the case of horizons of eluviation of the finer fraction lies between 300°C and 400°C while that of the coarser

fraction between 400°C and 500°C. In both the cases the maximum loss of moisture of horizons of illuviation lies between 400°C and 500°C. This could happen only when there is considerable admixture of clay minerals with hydrous micas and colloidal SiO<sub>2</sub>. The impurities present are far lower in the finer fraction than in the coarser separates. Besides the finer fraction alone shows the peculiar developmental characteristics of the horizons of illuviation and eluviation.

#### SUMMARY AND CONCLUSIONS

Clay samples having two particle diameters were studied in respect to their chemical composition and thermal dehydration characteristics. It is indicated that the clay composition and thermal characteristics of horizons of eluviation and illuviation are not similar when super fine clay is taken for studies. It is suggested that for all physical property determinations of clay samples, the particle size should be such as to clearly reflect the composition and characteristics of clay minerals of horizons of illuviation and eluviation. In the case of alluvial soil a particle size of less than 0.50 $\mu$  appears to be suitable for such studies.

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## PHOSPHATE FIXATION BY MINERALS IN ALKALINE MEDIUM

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Fixation of phosphate by soils, clays and clay minerals has been known for a long time. The reactions of phosphate with the sesquioxides of iron and aluminium either by solution and chemical precipitation or by surface adsorption have long been considered as important factors in the fixation of phosphorus in acid soil. More recently it has been found that phosphates also react with the silicate minerals in the soil.

Voelcker<sup>1</sup> showed that a sample of clay soil containing only a small percentage of  $\text{CaCO}_3$  was active in phosphate adsorption. He concluded that this was due to the formation of insoluble compounds with the hydrous iron and aluminium oxides present and to the consequent precipitation of calcium phosphate. A few years later Warrington<sup>2</sup> found that artificially prepared hydrous ferric oxide and alumina retained considerable amounts of phosphate from solution, even in presence of carbon dioxide.

In the last thirty years, an intensive study has been made of the reactions that take place between soil and phosphate ions and most of the work has been to elucidate the part played by iron and aluminium. These elements are found in most soils at least concentrated in the clay fraction. They both occur in the clay minerals themselves in octahedral linkage and aluminium is found also in tetrahedral linkage.

Despite a large number of investigations, however, the exact nature of the reactions of phosphate with the soil constituents is poorly understood perhaps due to the mutually contradictory or insufficient data obtained by various investigators on the following points :—

- (1) Whether kaolinite has any phosphate fixing capacity.
- (2) Which of montmorillonite or kaolinite has the higher phosphate fixing capacity.

The present work has been undertaken with a view to get some information on these points.

Black,<sup>3</sup> Murphy,<sup>4</sup> Scarseth<sup>5</sup> and Stout<sup>6</sup> have shown that phosphate fixation also takes place in clay minerals and this probably accounts for the phosphate that is fixed at about neutrality. So far most of the investigations on phosphate fixation were made only with kaolinite and montmorillonite. There seems to have been little or no study made of the phosphate retaining properties of other minerals. The present paper includes studies on phosphate fixation by a large number of clay and mica minerals besides kaolinite and montmorillonite like halloysite, natrolite, vermiculite, muscovite and biotite.

In the following discussion the terms adsorption, retention and fixation have been used synonymously and denote the removal of phosphate from the solution.



## EXPERIMENTAL

Phosphate fixation experiments were made on the minerals kaolinite, montmorillonite, halloysite, vermiculite, natrolite, muscovite and biotite at room-temperature (26°C), at a pH 11.8 and at 0.02, 0.0133, 0.01, 0.0033, 0.002 and 0.00125 molar concentrations of tripotassium phosphate.

Four grams of minerals were taken in stoppered flasks and treated with 100 c.c. of  $K_3PO_4$  solutions. The mixtures were then shaken in a mechanical shaker for an hour, kept for 48 hours and the supernatant liquid analyzed for  $P_2O_5$  content.

## RESULTS

TABLE No. 1

Phosphate fixation by Montmorillonite

Original concentration of $K_3PO_4$ (molarity)	Equilibrium concentration (molarity)	Phosphate adsorbed by 4 gm. mineral ( $P_2O_5$ in gm.)	Phosphate adsorbed by 100 gram mineral ( $P_2O_5$ in millimoles)
0.02000	0.00694	0.08905	15.660
0.01330	0.00391	0.06419	11.301
0.01000	0.00272	0.04959	8.730
0.00330	0.00136	0.01336	2.350
0.00200	0.00109	0.00617	1.080
0.00125	0.00081	0.00299	0.526

TABLE No. 2

Phosphate fixation by Kaolinite

0.02000	0.01822	0.01210	2.130
0.01330	0.01161	0.01155	2.035
0.01000	0.00900	0.00682	1.190
0.00330	0.00267	0.00432	0.760
0.00200	0.00174	0.00173	0.304
0.00125	0.00106	0.00148	0.253

TABLE No. 3

Phosphate fixation by Halloysite

0.02000	0.01830	0.01153	2.0290
0.01330	0.01212	0.00803	1.4100
0.01000	0.00890	0.00746	1.3100
0.00330	0.00258	0.00487	0.8570
0.00200	0.00175	0.00167	0.2940
0.00125	0.00102	0.00153	0.2690

TABLE No. 4  
Phosphate fixation by Natrolite

Original concentration (molarity)	Equilibrium concentration (molarity)	Phosphate adsorbed by 4 gram ( $P_2O_5$ in gm.)	Phosphate adsorbed by 100 gram ( $P_2O_5$ in millimoles)
0.02000	0.01805	0.01328	2.3300
0.01000	0.00877	0.00838	1.4700
0.00330	0.00277	0.00364	0.6408
0.00200	0.00181	0.00125	0.2200
0.00125	0.00114	0.00069	0.1210
0.00100	0.00092	0.00052	0.0910

TABLE No. 5  
Phosphate fixation by Vermiculite

0.02000	0.01153	0.05774	10.165
0.01330	0.00848	0.03293	5.797
0.01000	0.00611	0.02649	4.663
0.00330	0.00134	0.01345	2.367
0.00200	0.00093	0.00723	1.272
0.00125	0.00073	0.00353	0.621

TABLE No. 6  
Phosphate fixation by Muscovite

0.02000	0.01865	0.00915	1.6100
0.01330	0.01246	0.00572	1.0080
0.01000	0.00924	0.00513	0.9030
0.00330	0.00306	0.00165	0.2900
0.00200	0.00189	0.00074	0.1302
0.00125	0.00118	0.00041	0.0720

TABLE No. 7  
Phosphate fixation by Biotite

0.02000	0.01768	0.01582	2.780
0.01330	0.01201	0.00878	1.545
0.01000	0.00929	0.00432	0.848
0.00330	0.00289	0.00275	0.484
0.00200	0.00179	0.00144	0.253
0.00125	0.00108	0.00109	0.191

## DISCUSSION

The power of phosphate fixation of the various minerals in alkaline medium is relatively low and it appears from the results that montmorillonite has the highest value. Data presented here clearly show that the phosphate fixed at pH 11.8 by montmorillonite is 15 millimoles whereas by kaolinite it is about 2 millimoles. Vermiculite fixes about 10 millimoles and the other minerals fix as much phosphate as the kaolinite.

### *Mechanism of the Reactions with Minerals*

There are two types of reactions by which phosphate ions might be retained by the minerals :—

(1) By the formation of chemical bonds with lattice ions. Iron and aluminium are the only lattice ions that are likely to undergo a reaction with phosphate ions.

(2) By adsorption as  $\text{PO}_4'''$  and anion exchange.

In the light of recent investigations it seems rather difficult to distinguish between the phosphate fixation by chemical precipitation and adsorption. In some cases the high phosphate fixing capacity of the minerals can only be explained due to its precipitation by Fe, Al or Ca present in the system.

Adsorption of phosphate by kaolinite has been made use of in the study of anion exchange. Many authors have suggested replacement of OH ions by phosphate ions in kaolinite. Buswell and Dudenbostel<sup>7</sup> have supported this view on the basis of infra red absorption studies. Recently McAuliffe<sup>8</sup> Using deuterium tagged hydroxyls, have shown conclusively that the OH ions of clay mineral surfaces can enter into exchange reactions. Considerations of the structural arrangement of the hydroxyl ions in kaolinite suggest that the exchange between the phosphate ion in solution and the hydroxyl ions of the crystal lattice may account for the phosphate-fixing capacity of kaolinite but the high phosphate fixation by montmorillonite observed in this work and also reported by others cannot be accounted for from a consideration of the hydroxyl ions in the montmorillonite crystals. Montmorillonite has got a symmetrical structure. Each packet is composed of an octahedral gibbsite layer fused on both side with tetrahedral silica layers and so each face of the packet has a sheet of oxygen ions. The remaining hydroxyl ions of gibbsite sheet lying below the centre of the superposed hexagonal ring of oxygen ions, though available for exchange with ions of diameter smaller than oxygen, lie inaccessible to layer ions like the tetrahedral phosphate ion. Hence in the case of montmorillonite phosphate fixation seems to be due to its precipitation as insoluble phosphates. The hydroxyl ions present at the edges and corners of montmorillonite crystal are, however, available for exchange with  $\text{PO}_4$  ions.

Perkins,<sup>9</sup> Black and Low<sup>10</sup> and Sieling<sup>11</sup> have shown that kaolinite unless finely ground or subjected to chemical treatment that will break down its structure to give free alumina, possesses little capacity to fix phosphate. Using ground kaolinite that had been passed through a 100 mesh sieve, it was observed that it adsorbs very little phosphate in alkaline system. The small fixation by kaolinite may also be considered to be due to the small activity of its iron and aluminium at this high pH. At this high pH, phosphate may be fixed as insoluble calcium phosphate but this sample of kaolinite contains

very small amount of CaO and exchangeable calcium. So the possibility of the fixation of phosphate as insoluble calcium phosphate is eliminated. Whatever amount is adsorbed may be due to a process of exchange between phosphate ions of the solution and hydroxyl of the crystal lattice. Hence kaolinite fixes very small amount of phosphate, being 9.5 per cent. of the added phosphate.

Halloysite is also found to possess small phosphate fixing capacity. Here also the possibility of a reaction between aluminium and phosphate is precluded by a high pH value. The sample is also not rich in total and exchangeable calcium. So phosphate cannot be adsorbed through the intermediary of exchangeable calcium ions. It fixes only 2.024 millimoles of  $P_2O_5$  at 0.02 M phosphate concentration. Thus, it fixes 9.1 per cent. phosphate, almost equal to kaolinite. Halloysite has got a crystalline structure similar to kaolinite.

Montmorillonite is found to possess the highest phosphate fixing capacity in a highly alkaline medium. From the experimental results it is evident that it fixes 66.9 per cent. of the added phosphate from  $K_3PO_4$  solution.

Vermiculite retains about 47.9 per cent. of the added phosphate. The amount of phosphate fixed per 100 gram of oven-dried material increases from 0.61 millimoles to 10.15 millimoles with an increase in the concentration of added  $K_3PO_4$  from 0.00125 M to 0.02 M. Vermiculite resembles montmorillonite in its structure. It has an expanding structure and an unbalanced lattice with high base exchange capacity. Both montmorillonite and vermiculite contain appreciable amounts of CaO and exchangeable calcium. Phosphate from the solution reacts with the calcium in the material leading to the formation of tricalcium phosphate in the insoluble condition. Besides calcium, magnesium may also function to some extent in the fixation of phosphate.

Black reported that a sample of illite which contained free iron oxides absorbed up to 10 per cent. of the phosphate in 48 hours from a solution of 100 p.p.m. phosphorus at pH<sup>3</sup>. Perkins and King<sup>12</sup> found that muscovite fixed the largest amount of phosphate and the maximum fixation was at pH 3.5. From the above results it is clear that muscovite fixes 1.58 millimoles  $P_2O_5$  per 100 gram of material from a solution of 0.02 M phosphate concentration in 48 hours. It amounts to 6.7 per cent. of the phosphate. Biotite, on the other hand, fixed 2.78 millimoles which comes to 11.9 per cent. of the added phosphate. Thus biotite or black mica has got a greater phosphate fixing power than muscovite (white mica). It may be due to the presence of greater exchangeable calcium in biotite than muscovite. Biotite and muscovite contain 6.8 m.e. and 1.1 m.e. exchangeable calcium respectively. Exchangeable magnesium is also much greater in biotite than muscovite and Mg may also be effective in precipitating phosphate. There is evidence that phosphate ions can be fixed through exchangeable calcium.

Natrolite fixes 2.34 millimoles of  $P_2O_5$ , which amounts to 10.1 per cent. of the added phosphate, from a solution of 0.02M phosphate concentration in 48 hours.

Midgley<sup>13</sup> and also Mukherji and Ray Chaudhuri<sup>14</sup> working with kaolinite failed to observe any appreciable phosphate fixation.

From the preceding results, it is evident that phosphate fixation depends on a number of factors, which are as follows :—

(1) *Concentration of Phosphate ions in Solution.*—The course and the extent of the reaction of the added phosphate in silicate minerals is governed by the concentration. Phosphate fixation regularly decreases with a fall in phosphate concentration.

Deans and Rubins<sup>15</sup> and Ravikovitch<sup>16</sup> also showed the relation of concentration of phosphate and its fixation. Russell and Prescott<sup>17</sup>, Davis<sup>18</sup>, Kurtz<sup>19</sup> and Low and Black<sup>20</sup> demonstrated that the adsorption agreed with the Freundlich adsorption equation.

(2) *Type of Mineral*.—Phosphate fixation varies in different minerals. Some minerals have a large capacity to fix phosphates while others show a small phosphate fixing capacity. The amount of phosphate fixed from a phosphate solution depends a good deal on the nature of the mineral. Thus montmorillonite and vermiculite can fix large amount of phosphate while biotite, kaolinite, halloysite, natrolite and muscovite can fix only moderate amounts of phosphate at pH 11.8. In general, the order in which the minerals fix phosphate under the experimental conditions is montmorillonite > vermiculite > biotite > natrolite > kaolinite > halloysite > muscovite.

(3) *Effect of Exchangeable cations*.—Of the many reactions suggested for phosphate fixation one is this that phosphate can be adsorbed through the intermediary of exchangeable calcium ions. Demolon and Barbier<sup>21</sup> were the first to put forward this view. Even at low pH levels below neutrality, where calcium precipitation cannot be expected, Ca-clays retain more phosphate than do Na, NH<sub>4</sub> or K-clays. Scarseth<sup>22</sup> suggested that this additional retention is due to a linking of phosphate to the colloid through a Ca ion on the exchange complex. Whether this additional retention is a precipitation of a calcium phosphate at the surface or that the exchangeable calcium ions act as bridges between the phosphate ions and the clay surface is not clear, but it is quite definite that the exchangeable calcium ions play a very important part in the phosphate fixation by these clay minerals under the present experimental conditions. This is why montmorillonite and vermiculite which have a high exchangeable calcium possess a high phosphate fixing ability.

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# ADSORPTION OF COPPER FROM ACID SYSTEMS BY MINERALS

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The reactions of cupric ions in soils are much complicated due to the following reasons :—

- (1) The precipitation of cupric hydroxide and cupric-carbonate under conditions that generally exist in neutral or calcareous soils.
- (2) The formation of cupric hydroxy ions when absorbed on layer silicates.
- (3) The formation of complexes of copper with organic compounds of the soil.

The availability to plants of native or applied copper is greatly influenced by these three types of reactions. Majority of workers such as Lees,<sup>1</sup> Antipov Karataev,<sup>2</sup> Steenbjerg,<sup>3</sup> Vermaat,<sup>4</sup> Lucas,<sup>5</sup> and Svenberg,<sup>6</sup> have investigated the role of organic matter in copper fixation and they favour the view that organic matter because of its high copper fixing property, is responsible for the low availability of this nutrient in organic soils. Svenberg observed that the fixation of copper in soils is a function of organic matter. Allison<sup>7</sup> reported that the copper fixing power of peats was so great, that an application of 10,000 lbs of copper sulphate caused but a temporary injury.

Although some work has been done on the role of organic matter in copper fixation, but no detailed experiments have, so far, been reported on the adsorption of copper by inorganic materials. The present study was, therefore, restricted to inorganic exchange systems. Exchange reactions of copper, calcium, potassium and hydrogen ions with montmorillonite, kaolinite, etc. were carried out in acid systems to characterize the adsorption of copper as hydroxylated copper ions in the absence of precipitation of cupric hydroxide.

## EXPERIMENTAL

Stock supplies of the minerals were used without purification. All the minerals were finely powdered and sieved through 100 mesh screen. Montmorillonite was obtained for Kashmir, kaolinite from Madhya Pradesh, vermiculite from Mysore and the rest from Ward's Natural Science Establishment, Inc. from U. S. A.

### *Preparation of calcium and potassium saturated montmorillonite, kaolinite and halloysite*

The derivatives were prepared by treating the natural mineral with normal  $\text{CaCl}_2$  and  $\text{KCl}$  respectively a number of times till the other cations failed to appear in the filtrate. The free electrolytes were then removed by exhaustive leaching with water. For adsorption experiments two grams of minerals or their derivatives were taken in well corked flasks and 100 c.c. of  $\text{CuSO}_4$  solutions of varying

concentrations were added and the contents were shaken for an hour and then allowed to stand for 48 hours. The supernatant liquid was then analyzed for copper, calcium and potassium.

*Determination of copper.*—Copper was estimated iodometrically using hypo-solution.

*Separation of copper from calcium and potassium* —Copper interferes in the estimation of calcium as copper oxalate is insoluble. Copper was first removed by passing slowly  $H_2S$  gas and then boiling off  $H_2S$  from the solution. Calcium was precipitated as oxalate and estimated volumetrically. For the determination of potassium, the solution was first freed from cupric ions and then potassium was estimated by cobaltinitrite method.

*pH measurements.*—pH of the supernatant liquids were measured electrometrically by Beckman pH meter.

## RESULTS

TABLE No. 1

Adsorption of copper by Ca-Montmorillonite and exchange of Calcium

Normality of $CuSO_4 \cdot 5H_2O$ Solution	Copper added (m.e./100 gm)	Copper adsorbed (m.e./100 gm)	Calcium exchanged (m.e./100 gm)	Original pH of the solution	Equilibrium pH of the solution
0.1000	500.0	98.02	120.00	3.0	3.2
0.0400	200.0	62.85	76.00	3.3	3.6
0.0200	100.0	45.01	72.10	3.4	3.9
0.0133	66.7	35.99	68.85	3.5	4.1
0.0100	50.0	34.01	58.72	3.6	4.3
0.0033	16.7	26.39	44.81	3.9	4.6

TABLE No. 2

Adsorption of copper by Ca-Kaolinite and exchange of Calcium

Normality of $CuSO_4 \cdot 5H_2O$ solution	Copper added (m.e./100 gm)	Copper adsorbed (m.e./100 gm)	Calcium exchanged (m.e./100 gm)
0.10	500	12.5	13.90
0.04	200	10.4	11.01
0.02	100	5.9	6.00
0.01	50	5.4	5.76



TABLE No. 3

Adsorption of copper by K-Montmorillonite and exchange of Potassium ions

Normality of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution	Copper adsorbed (m.e./100 gm.)	Potassium released (m.e./100 gm.)	Original pH of the solution	Equilibrium pH of the solution
0.10	108.52	87.21	3.0	3.8
0.04	79.60	68.09	3.3	4.1
0.02	68.61	58.50	3.4	4.3
0.01	60.80	49.32	3.6	4.5

TABLE No. 4

Adsorption of copper by K-Kaolinite and exchange of Potassium ions

0.10	13.98	10.37	3.0	2.6
0.04	11.67	9.63	3.3	2.9
0.02	10.04	8.12	3.4	3.1
0.01	8.43	6.79	3.6	3.4

TABLE No. 5

Adsorption of copper K-Halloysite and exchange of Potassium ions

0.10	21.86	17.14	3.0	3.4
0.04	18.24	13.93	3.3	3.6
0.02	16.89	11.87	3.4	3.9
0.01	11.95	8.14	3.6	4.2

TABLE No. 6

Adsorption of Copper by Muscovite

Normality of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution	Copper added (m.e./100 gm.)	Copper adsorbed (m.e./100 gm.)	Original pH of the solution	Equilibrium pH of the solution
0.10	500	12.10	3.0	3.2
0.04	200	5.03	3.3	3.7
0.02	100	3.87	3.4	4.0
0.01	50	2.72	3.5	4.2

TABLE No. 7  
Adsorption of copper by Vermiculite

Normality of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution	Copper added (m. e./100 gm)	Copper adsorbed (m. e./100 gm)
0.1000	500.0	29.8
0.0400	200.0	25.9
0.0200	100.0	25.0
0.0133	66.7	23.9
0.0100	50.0	20.2
0.0033	16.7	6.8

TABLE No. 8  
Adsorption of copper by Biotite

0.1000	500.0	24.01
0.0400	200.0	16.82
0.0200	100.0	10.24
0.0133	66.7	9.10
0.0100	50.0	7.86

#### DISCUSSION

The foregoing results on the adsorption of copper by various silicate minerals clearly show that copper is being adsorbed from a copper sulphate solution. The adsorption of copper is much greater in montmorillonite than that in kaolinite. The mica minerals muscovite and biotite show little tendency to take up copper ions from acid solutions.

It is well-known that kaolinite possesses a characteristic crystalline structure in which the sheet distances remain constant and the exchange reactions with the usual electrolytes can take place only on the surface of the separate particles; the total charge carried by this surface is relatively small consequently the adsorption capacity of kaolinite in relation to electrolytes is very small, while montmorillonite, according to the latest investigations, has a mobile structure and in a series of liquids swells along the c-axis. From this fact it may be concluded that montmorillonite can adsorb cations with its inner surface as well as with the outer one. Actually the adsorbing capacity of montmorillonitic clays is many times that of kaolin-clays.

### *Nature of Copper ions adsorbed from a solution of copper sulphate*

A perusal of the aforementioned results shows that there are three trends in the data regarding the relationship between the copper adsorbed and the ions released.

(1) pH increased and Cu adsorbed  $<$  Ca released.

(2) pH increased and Cu adsorbed  $>$  K released.

(3) pH decreased and Cu adsorbed  $>$  K released.

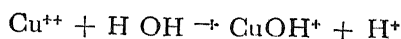
Thus there are two important features of the exchange of cupric ions.

(1) The change in pH during the reaction.

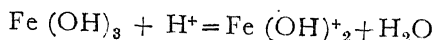
(2) The inequality between potassium and calcium released and copper adsorbed.

In view of the data presented in Tables (1) and (2), the adsorption of hydrogen ions by the clay seems quite possible, thus increasing the pH of the solution. The release of calcium ions exceeds the adsorption of copper, corresponding to the amount of hydrogen adsorbed. The trend (2) and (3) in the data may be explained by adsorption of copper as the monovalent cupric hydroxy ion.

Spencer and Gieseking<sup>8</sup> recently studied the adsorption of cobalt by Ca-Amberlite and Ca-Swygert clay. They found that the cobalt was adsorbed mainly as the monovalent cobaltous-hydroxy ion. This conclusion logically follows from the results (Tables 3, 4 and 5) which show that the amount of  $\text{Cu}^{++}$  adsorbed by the K-clays is greater than the amount of  $\text{K}^+$  replaced. The probable equilibrium that exists in a solution of copper sulphate in presence of potassium saturated montmorillonite may be as follow :—



This reaction releases hydrogen ions and so the solution pH is decreased. When hydroxy cupric ion  $[\text{Cu}(\text{OH})^+]$  is adsorbed on the clay minerals, only one milliequivalent of potassium is released, although two milliequivalents of copper are adsorbed. Increase of the solution pH (Tables 3 and 5) inspite of the liberation of hydrogen ions by cupric hydrolysis shows that some buffer is dissolving. It seems that iron is being dissolved from the mineral lattice and it buffers the solution.



In these experiments iron was actually found in the solution. The reported liberation of  $\text{H}^+$ ,  $\text{Al}^{+++}$  and  $\text{Fe}^{+++}$  from pure clay minerals on repeated salt treatment by Mukherji and Chatterji<sup>9</sup> lends support to this explanation. Menzel and Jackson<sup>10</sup>, while studying the adsorption of the copper, were unable in all cases to obtain a decrease in pH accompanying the adsorption of the cupric hydroxy ions. They postulated that the H ions produced during the hydrolysis were buffered by aluminium dissolved from the clay minerals.

Thus it seems quite probable that some such buffer system is operating in the copper adsorption on montmorillonite, etc., in the present investigation.

#### SUMMARY

1. Copper adsorption takes place in different minerals to different extent. The adsorption is greater in montmorilloite than kaolinite. The mica minerals muscovite and biotite are able to adsorb copper only to a very little extent.

2. Either copper is adsorbed as  $\text{Cu}^{++}$  ion and the simple type of exchange adsorption of cupric and hydrogen ions with the release of complementary ion from the cation exchange system takes place.

3. Copper is adsorbed as monovalent hydroxy-cupric ion as indicated by the release of less K than Cu adsorbed.

4. Iron acts as a buffer, thus explaining the increase in pH.

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## POTASSIUM FIXATION UNDER WET AND ALTERNATE WET AND DRY CONDITIONS BY CLAY MINERALS

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It is well-known that certain cations may be adsorbed by clay minerals in a difficultly exchangeable state. Potassium, ammonium and rubidium are amongst such ions but potassium, in view of its value in soil fertilization, has been mostly studied. The occurrence of potassium fixation in soils and clays has been demonstrated by many workers and it has generally been observed that after the application of heavy doses of potassium fertilizers to soils, fixation of potassium takes place in certain soils but not in others. Volk<sup>1</sup> attributed this fixation to the development of mica under these conditions. Many different theories have, since, been presented to explain this phenomenon. It has been shown rather conclusively that fixation occurs in the fine clay fraction of 2:1 type clay minerals. Page and Baver<sup>2</sup> have proposed a mechanism which explains the fixation of potassium as due to entrapment of the exchangeable potassium in the voids in dehydrated montmorillonite minerals. Amongst the earlier workers special mention may be made of Frear and Erb,<sup>3</sup> Page and Williams,<sup>4</sup> Chaminade,<sup>5</sup> Joffe and Kolodny.<sup>6</sup>

Whether drying the clay mineral is necessary to produce fixation is a matter of controversy. It has been shown in a number of papers by various authors that small amounts of potassium are fixed in clay minerals without drying. Martin,<sup>7</sup> Attoe<sup>8</sup> and Stanford<sup>9</sup> have shown that potassium fixation may occur with or without drying. Wood and DeTurk,<sup>10</sup> Bray and DeTurk<sup>11</sup> and others have shown that illite will fix potassium, and most of the  $K^+$  fixed in soils is probably due to the action of this clay mineral. Barshad<sup>12</sup> has shown that vermiculite can fix some potassium.

Thus, there appears to be two distinct kinds of inorganic fixation, one brought about by drying and the other taking place even in continuously moist conditions. The present investigation was undertaken with a view to make a comparative study of potassium fixation by kaolinite, halloysite and montmorillonite under wet conditions and under conditions of alternate wetting and drying.

### EXPERIMENTAL

Stock supplies of the minerals were used without purification. All the minerals were finely powdered and passed through 100 mesh sieve. Montmorillonite was obtained from Kashmir, kaolinite from Madhya Pradesh and halloysite from Ward's Natural Science Establishment, Inc. from U. S. A.

The experiments of potassium fixation under wet condition were carried out in the following way :—

Four grams of kaolinite, halloysite and montmorillonite were treated with  $K_3PO_4$  solutions of varying concentrations, shaken for two hours in an automatic shaker, kept for two days and filtered through a buchner funnel. The clear filtrate was analyzed for potassium. Potassium was estimated as cobaltinitrite. Exchangeable potassium was determined in the treated clay minerals by leaching the sample with neutral normal ammonium acetate and estimating the potassium in the leachate. The potassium that could not be replaced by neutral normal ammonium acetate was taken to be the fixed potassium under wet conditions.

The potassium fixation under alternate wet and dry conditions was studied according to the following procedure :—

The clay minerals were treated with molar solutions of  $K_2HPO_4$  ( $pH > 8$ ).  $K_2HPO_4$  was chosen in order to study the interaction between potassium salts and clay minerals in a slightly alkaline medium because Noll's <sup>13</sup> work on the synthesis of clay minerals indicates that the formation of illite and consequently fixation of potassium is favoured in a slightly alkaline medium. The mixtures were evaporated to dryness on a waterbath. Sufficient water was then added to dissolve the potassium salt and again evaporated to dryness on a waterbath. This sequence of operations was repeated every day for thirty days and at the end of this period, the mixtures were exhaustively leached with water and then with 0.04 N HCl to convert the potassium clays into hydrogen clays (H-clays). Finally, the H-clays were washed free of acid by repeated leaching with distilled water. The potassium contents of the H-clays prepared from the untreated as well as  $K_2HPO_4$  treated clays were then determined by the cobaltinitrite method after fusing the clays with sodium carbonate. The results obtained in these experiments have been detailed in the following tables :—

## RESULTS

### Potassium fixation by Kaolinite

TABLE No. 1

Original concentration of $K_3PO_4$ (molarity)	Equilibrium concentration (molarity)	Amount of $K_2O$ adsorbed by 4 gm mineral (mgm)	Amount of $K_2O$ adsorbed (m. e./100 gm)	Amount of potassium replaceable by neutral $NCH_3COONH_4$ (m.e./100 gm)
0.02000	0.0159	45.290	24.09	24.12
0.01330	0.0108	24.420	12.98	12.98
0.01000	0.0084	17.450	9.28	9.28
0.00330	0.0023	10.633	5.65	5.65
0.00200	0.0014	5.782	3.07	3.12
0.00125	0.0009	3.199	1.69	1.68

TABLE No. 2  
Potassium fixation by Halloysite

Original concentration of $K_3PO_4$ (molarity)	Equilibrium concentration (molarity)	Amount of $K_2O$ adsorbed by 4 gm (mgm.)	Amount of $K_2O$ adsorbed (m.e./100 gm)	Amount of potassium replaceable by neutral $N CH_3 COONH_4$ (m.e./100 gm)
0.02000	0.0150	54.174	28.81	28.86
0.01330	0.0097	37.416	19.89	19.89
0.01000	0.0071	32.626	17.35	17.35
0.00330	0.0020	13.668	7.26	7.28
0.00200	0.0012	8.491	4.51	4.51
0.00125	0.0009	3.901	2.07	2.07

TABLE No. 3  
Potassium fixation by Montmorillonite

0.02000	0.00500	165.734	88.15	87.97
0.01330	0.00300	112.490	59.83	59.78
0.01000	0.00210	87.020	46.28	46.28
0.00330	0.00076	28.465	15.13	15.13
0.00200	0.00051	16.523	8.78	8.74
0.00125	0.00030	10.505	5.58	5.58

TABLE No. 4  
Potassium fixation by clay minerals under conditions of alternate wetting and drying

Clay mineral	Amount of $K_2O$ in H-mineral prepared from the original sample in m. e./100 gram	Amount of $K_2O$ in H-mineral from the treated sample (m. e./100 gram)	Amount of potassium fixed expressed as $K_2O$ in m. e./100 gram
Kaolinite	1.744	1.744	Nil
Halloysite	0.000	0.000	Nil
Montmorillonite	12.382	21.680	9.298

## DISCUSSION

A perusal of the results recorded in Tables 1, 2 and 3 clearly show that when  $K_3PO_4$  of concentrations 0.02M—0.00125M is added and allowed to remain in contact with clay minerals for two days, no fixation of potassium takes place in either of the minerals. The clay minerals adsorb appreciable amounts of potassium but all the potassium adsorbed by this treatment is subsequently replaced by ammonium acetate. Although montmorillonite adsorbs 88.15 m. e. of potassium but only 0.18 m. e. (which is negligible) remains in a non-exchangeable state. It is clear, therefore, that no crystal lattice cation fixation takes place under these experimental conditions.

It is, however, apparent from the data presented in this work that under alternate wet and dry conditions, montmorillonite can fix a considerable amount of potassium when the mineral is treated with a large amount of potassium salts in a slightly alkaline medium. Kaolinite and halloysite have absolutely no power to fix K even under these conditions. Joffe and Levine have, however, reported  $K^+$  fixation by very finely ground kaolinite, but the grinding may well have destroyed the kaolinite structure. According to Reney and Hoover<sup>14</sup> montmorillonite has some power to fix  $K^+$

Soils contain different clay minerals and it is quite possible that conversion of some clay minerals into potassium bearing clay minerals, such as illite, may take place under these conditions while this change may not take place with other clay minerals. The lattice structures of clay minerals are thus likely to play a prominent role in potassium fixation. One clay mineral may be transformed into another, if the crystalline structures of the two minerals are fundamentally similar. Chatterji<sup>15</sup> found that in presence of large amounts of potassium salts, montmorillonites are transformed into illite.

A consideration of the lattice structures of these minerals also shows that such a change is not possible with kaolinite and halloysite. In montmorillonite, a gibbsite sheet is enclosed between two silica units with vertices pointing towards each other (Hofmann, Endell and Wilm).<sup>16</sup> The lattice structure of illite is very much similar, the only difference being that in illite about 15% of the  $Si^{+++}$  positions are occupied by  $Al^{+++}$  in the silica tetrahedral sheets and the resulting negative charge is balanced by  $K^+$  ions which fit into the hexagonal gaps of oxygen atoms and serve to bind the layer packets together (Grim, Bray and Bradley).<sup>17</sup> The kaolinite and halloysite structures, on the other hand, consist of a gibbsite sheet fused to a single silica sheet.

Although, no attempt here was made to find out the percentage of montmorillonite converted into illite, yet it appears from a consideration of the lattice structures of the minerals that failure to fix any potassium by kaolinite and halloysite and appreciable fixation by montmorillonite is due to the conversion of latter into illite and the former remaining as such.

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FIXATION OF ATMOSPHERIC NITROGEN UNDER STERILE  
CONDITIONS ON KAOLINITE WITH STRAW AND  
COWDUNG AND THE EFFECT OF DIFFERENT  
PHOSPHATES ON THE EFFICIENCY  
OF FIXATION

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The problem of nitrogen transformation in soils and other surfaces was first thought to be entirely a biological phenomenon due possibly to the enzymes present in the micro-organisms. Nitrogen fixation in the absence of bacterial activity is also well established. Dhar and coworkers<sup>1</sup> have put forward substantial claims to explain the phenomenon from purely a physico-chemical view point. They have done systematic work under sterile conditions both with soil and pure oxides and have obtained a large number of results showing the photochemical nature of the process. Ranjan and Bhattacharya<sup>2</sup> have also obtained evidence in favour of nitrogen fixation under sterile conditions with molasses as energy material.

The fixation of this type of nitrogen has been extensively studied for over twenty years in the Chemical Laboratories and Sheila Dhar Institute of Soil Science of the Allahabad University. It has been established from these researches that when different energy materials like sugars, starch, cellulose, glycerol, fats, peat, lignite, etc., are mixed with soil or sand and are allowed to undergo slow oxidation, the concentration of carbon decreases, but there is a concomitant increase in the nitrogen of the system both under sterile and unsterile conditions.

Although Dhar has done a large number of experiments on the nitrogen fixation under sterile conditions in soils, sands and even in pure oxides but so far, no detailed experiments have been reported on this type of fixation in pure clay minerals. The present work was undertaken to study the nitrogen fixation on the surface of kaolinite from a physico-chemical view point and also to see the effect of different phosphates on this process.

EXPERIMENTAL

Five grams of powdered and oven-dried kaolinite were placed in 35 c.c. glass test-tubes. The energy materials were added at the rate of 1% carbon. The energy materials (straw and cowdung) were thoroughly mixed with the mineral in the tubes and test-tubes were plugged with cotton wool after adding 10 c.c. of distilled water to each test-tube. The test-tubes were then sterilized in an autoclave under 15-20 lbs pressure for one hour after which one set was exposed to light from an electric bulb

(100 watts) and another corresponding set kept in the dark covered with a thick black cloth. The test-tubes were all arranged in wooden trays and the average distance of the tubes from the bulb was 3-4 feet approximately. The total volume of the solution in each case was kept to 10 c. c. and two different sets of test-tubes were put for the first and second readings. The concentration of the phosphate in all cases was 0.25 gram  $P_2O_5$  per 100 gram of the mineral surface.

For the purpose of estimations in these sterile sets, the solution in the test-tubes was carefully evaporated to dryness on a waterbath with a few drops of dilute  $H_2SO_4$  to check any loss of ammonia and then the whole test-tube along with the dried mass was broken into a Kjeldhal flask and finally charred with conc.  $H_2SO_4$  for the estimation of total carbon and total nitrogen. The total carbon in the kaolinite, straw and cowdung was estimated by the method of Robinson, McLean and Williams.<sup>3</sup> The total nitrogen was estimated by salicylic acid reduction method.<sup>4</sup> The chemical analysis of the mineral was done by sodium carbonate fusion method as described by Washington.<sup>5</sup> The analysis of plant materials was done according to the method given in Pipers<sup>6</sup> book on Soil and Plant Analysis.

## RESULTS

TABLE No. 1

### Analysis of Kaolinite

	%
$SiO_2$	63.9000
$Al_2O_3$	27.6000
$Fe_2O_3$	1.4000
$P_2O_5$	0.1400
$K_2O$	...
$MgO$	0.8330
$CaO$	0.4900
C	0.1147
N	0.0034

TABLE No. 2

### Analysis of Straw and Cowdung

	Straw %	Cowdung %
Moisture	3.9400	4.9000
Loss on Ignition	88.0000	63.4600
Ash	11.9900	36.5300
$SiO_2$	7.0700	30.6600
$CaO$	0.7840	2.5200
$MgO$	0.2100	0.9342
$K_2O$	1.6618	0.7216
$P_2O_5$	0.2925	0.6729
Total Carbon	36.6900	28.6200
Total Nitrogen	0.5112	11.0108

TABLE No. 3  
Kaolinite + Straw

Period of exposure in days	Total carbon in the system %	<i>Light</i>			
		Carbon oxidized %	Total nitrogen %	Nitrogen fixed %	Efficiency
0	1.0851	—	0.01687	—	—
210	0.9236	0.1615	0.01963	0.00276	17.09
315	0.7971	0.2880	0.02172	0.00485	16.84
<i>Dark</i>					
0	1.0851	—	0.01687	—	—
210	0.9670	0.1181	0.01783	0.00096	8.18
315	0.8426	0.2425	0.01877	0.00190	7.90

TABLE No. 4  
Kaolinite + Straw + Ca (H<sub>2</sub> PO<sub>4</sub>)<sub>2</sub> H<sub>2</sub>O

<i>Light</i>					
0	1.07940	—	0.01677	—	—
210	0.89270	0.18670	0.02012	0.00335	17.95
315	0.72991	0.34949	0.02297	0.00620	17.74
<i>Dark</i>					
0	1.07940	—	0.01677	—	—
210	0.93340	0.1460	0.01806	0.00129	8.78
315	0.76090	0.3185	0.01951	0.00274	8.62

TABLE No. 5  
Kaolinite + Straw + FePO<sub>4</sub>

<i>Light</i>					
0	1.0794	—	0.01677	—	—
210	0.9140	0.1654	0.01972	0.00295	17.87
315	0.7711	0.3083	0.02215	0.00538	17.45
<i>Dark</i>					
0	1.0794	—	0.01677	—	—
210	0.9551	0.1243	0.01784	0.00107	8.66
315	0.7943	0.2851	0.01918	0.00241	8.46

TABLE No. 6  
Kaolinite + Straw +  $\text{AlPO}_4$

*Light*

Period of exposure in days	Total carbon %	Carbon oxidized %	Total nitrogen %	Nitrogen fixed %	Efficiency
0	1.07940	—	0.01677	—	—
210	0.91770	0.16170	0.01961	0.00284	17.54
315	0.78154	0.29786	0.02193	0.00516	17.32

*Dark*

0	1.07940	—	0.01677	—	—
210	0.95930	0.12010	0.01778	0.00101	8.38
315	0.81612	0.26328	0.01895	0.00218	8.28

TABLE No. 7  
Kaolinite + Straw + Magnesium phosphate

*Light*

0	1.0788	—	0.01678	—	—
210	0.8965	0.1823	0.02002	0.00326	17.91
320	0.7523	0.3265	0.02250	0.00574	17.58

*Dark*

0	1.0788	—	0.01676	—	—
210	0.9375	0.1413	0.01798	0.00122	8.69
320	0.7704	0.3084	0.01935	0.00259	8.41

TABLE No. 8  
Kaolinite + Straw +  $\text{CaHPO}_4$

*Light*

0	1.07880	—	0.01676	—	—
210	0.85520	0.22420	0.02277	0.00601	26.79
320	0.72035	0.35845	0.02607	0.00931	25.97

*Dark*

0	1.07880	—	0.01676	—	—
210	0.90540	0.17340	0.01918	0.00242	13.98
320	0.75240	0.32640	0.02077	0.00401	12.31

TABLE No. 9

Kaolinite + Straw + Tricalcium phosphate

*Light*

Period of exposure in days	Total carbon %	Carbon oxidized %	Total nitrogen %	Nitrogen fixed %	Efficiency
0	1.0794	—	0.01677	—	—
210	0.8368	0.2426	0.02194	0.00517	21.33
320	0.7120	0.3674	0.02439	0.00762	20.74

*Dark*

0	1.0794	—	0.01677	—	—
210	0.8722	0.2072	0.01873	0.00196	9.47
320	0.7405	0.3389	0.01989	0.00312	9.23

TABLE No. 10

Kaolinite + Cowdung

*Light*

0	1.0759	—	0.03732	—	—
180	0.8642	0.2117	0.04080	0.00348	16.57
285	0.7377	0.3382	0.04263	0.00536	15.86

*Dark*

0	1.0759	—	0.03732	—	—
180	0.8931	0.1828	0.03877	0.00145	7.97
285	0.7976	0.2783	0.03941	0.00209	7.52

TABLE No. 11

Kaolinite + Cowdung +  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ *Light*

0	1.0714	—	0.03716	—	—
180	0.8518	0.2196	0.04105	0.00389	17.74
285	0.6820	0.3894	0.04403	0.00687	17.64

*Dark*

0	1.0714	—	0.03716	—	—
180	0.8808	0.1906	0.03875	0.00159	8.38
285	0.7416	0.3298	0.03990	0.00274	8.31

TABLE No. 12  
Kaolinite+Cowdung+FePO<sub>4</sub>

<i>Light</i>					
Period of exposure in days	Total carbon in the system %	Carbon oxidised %	Total nitrogen %	Nitrogen fixed %	Efficiency
0	1.0703	—	0.03713	—	—
180	0.8550	0.2153	8.04078	0.00365	16.97
285	0.7091	0.3612	0.04327	0.00614	16.99
<i>Dark</i>					
0	1.0703	—	0.03713	—	—
180	0.8840	0.1863	0.03870	0.00157	8.42
285	0.7750	0.4953	0.03959	0.00246	8.36

TABLE No. 13  
Kaolinite+Cowdung + AlPO<sub>4</sub>

<i>Light</i>					
0	1.0714	—	0.03716	—	—
180	0.8583	0.2131	0.04072	0.00356	16.72
285	0.7246	0.3468	0.04287	0.00371	16.43
<i>Dark</i>					
0	1.0714	—	0.03716	—	—
180	0.8866	0.1848	0.03865	0.00149	8.10
285	0.7865	0.2849	0.03941	0.00225	7.90

TABLE No. 14  
Kaolinite+Cowdung+MgHPO<sub>4</sub>

<i>Light</i>					
0	1.0709	—	0.03715	—	—
180	0.8526	0.2183	0.04090	0.00375	17.21
285	0.7003	0.3706	0.04367	0.00652	17.60
<i>Dark</i>					
0	1.0709	—	0.03715	—	—
180	0.8896	0.1813	0.03870	0.00155	8.24
285	0.7585	0.3124	0.03978	0.00263	8.43

TABLE No. 15  
Kaolinite + Cowdung +  $\text{CaHPO}_4$

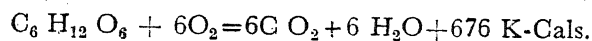
<i>Light</i>					
0	1.0709	—	0.03715	—	—
180	0.8151	0.2558	0.04264	0.00549	21.47
285	0.6527	0.4182	0.04602	0.00887	21.21
<i>Dark</i>					
0	1.0709	—	0.03715	—	—
180	0.8422	0.2287	0.03949	0.00234	10.25
285	0.7297	0.3412	0.04056	0.00341	10.01

TABLE No. 16  
Kaolinite + Cowdung +  $\text{Ca}_3(\text{PO}_4)_2$

<i>Light</i>					
0	1.0714	—	0.03716	—	—
180	0.8111	0.2603	0.04210	0.00494	19.01
285	0.6283	0.4431	0.04553	0.00837	18.90
<i>Dark</i>					
0	1.0714	—	0.03716	—	—
180	0.8420	0.2294	0.03928	0.00212	9.23
285	0.7130	0.3584	0.04036	0.00320	8.93

#### DISCUSSION

The foregoing results clearly show that nitrogen fixation in kaolinite can take place in the complete absence of micro-organisms both in presence of light and in the dark, provided there is a source of energy available to the system from slow oxidation of the energy material. It is clear, therefore, that on the surface of kaolinite the energy materials undergo slow oxidation at the ordinary temperature by the oxygen adsorbed on the surface because the carbon of the system steadily decreases with time. The carbon of the organic matter is finally oxidized in the system to carbon dioxide and a considerable amount of energy is liberated.



The energy<sup>7</sup> thus liberated is utilized in the endothermic reaction by which the atmospheric nitrogen is fixed. The mechanism of nitrogen fixation process seems to be through the decomposition of water molecule into atomic hydrogen and hydroxyl radical by absorption of energy obtained from the oxidation of carbonaceous matter. The energy relationships involved in the process of nitrogen fixation are as follows:—

1.  $\text{H}_2\text{O} + 112 \text{ K Cals.} = \text{H} + \text{O H}$
2.  $6\text{H} + \text{N}_2 = 2\text{NH}_3$



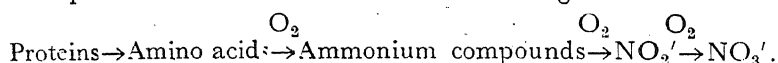
It is well-known that in absence of moisture, nitrogen fixation does not take place because water plays a vital role in this process as postulated in the above mechanism. The ammonia readily undergoes oxidation and forms nitrite and finally nitrate. Light plays an important role in this process of nitrogen fixation as it is absorbed in the system and thus supplies additional energy for these reactions to proceed.

With these energy materials (straw and cowdung) it is seen that even in sterile sets the effect of light is very marked. The velocity of carbon oxidation and the efficiency of nitrogen fixation is definitely much greater (nearly double) in the exposed sets than in those covered with a black cloth, thus favouring the photo-chemical viewpoint.

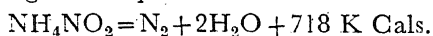
It is evident from the foregoing results that the addition of different phosphates to kaolinite plus organic matter favours the oxidation of the organic matter both in light and dark. Phosphate is one of the chief plant nutrients and is an important constituent of manures and fertilizers. Bear<sup>8</sup> has remarked that within limits phosphate fertilizers together with potash salts and lime can be substituted for nitrogen-fertilizers. Their use stimulates the nitrogen fixation bacteria both symbiotic and non-symbiotic to a greater activity.

It seems that phosphates play a vital role in the improvement and maintenance of the nitrogen status of the soils. The proteins that are present in the humus are likely to be stabilized by the formation of the nucleoproteins, phosphoproteins, etc., with the combination of proteins and phosphates or other substances. In this connection the following lines from Sir John Russell's<sup>9</sup> book are of interest: "It is not known in what form phytin and nucleic acid occur in the organic matter, though, presumably most of the nucleic acid must be in nucleoproteins or in which humic fractions they are concentrated. They must be protected in some way from the soil enzymes as they are readily dephosphorylated if mixed with the soil, *i. e.*, they have their groups split off as inorganic-orthophosphate anions. This is also shown independently by the fact that these organic phosphates can only be extracted in good yield from the humic material if it is subjected to fairly drastic pre-treatment."

Moreover, the organic matter added to kaolinite undergoes slow oxidation on its surface aided by sunlight or artificial light, and fixes nitrogen of the air and forms proteins in this process. Under ordinary conditions the proteins formed undergo ammonification and nitrification which are also accelerated by light absorption and form nitrate as in the following scheme.



In this series of reactions the unstable substance ammonium nitrite is formed and decomposed according to the equation :



Hence along with nitrogen fixation and formation of proteins due to the oxidation of energy materials, ammonification and nitrification, which oppose the increase of proteins in the soil, take place and thus the amount of protein remaining in the soil tends to decrease. Hence the apparent efficiency of nitrogen fixation *i.e.*, the amount of nitrogen in milligrams fixed per gram of carbon oxidized, appears to fall off when ammonification and nitrification take place. But in presence of large amounts of phosphate in the system more or less stable phospho-

proteins are formed by the combination of proteins and phosphorus compound. These compounds seem to resist nitrification and ammonification and loss of nitrogen better than proteins alone. This seems to be an important reason why the efficiency of nitrogen fixation appears larger in presence of increasing quantities of phosphates.

The highest efficiency has been recorded with dicalcium phosphate. Tricalcium phosphate has a higher efficiency of nitrogen fixation than monocalcium phosphate. Iron and aluminium phosphates have almost an equal effect on nitrogen fixation having the lowest efficiency. The experimental results recorded in this paper show that in kaolinite, nitrogen fixation of the order of 4.85 to 9.31 milligrams in light and 1.9 to 4.01 milligrams in dark has been observed. Hence there is a marked light effect in these experiments on nitrogen fixation.

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